Antoine Laurent Lavoisier (1743–1794)

Famous for his care in quantitative experiments, for demonstrating the true nature of combustion, for introducing system into the naming and grouping of chemical substances. Executed (1794) during the French Revolution because of his connection with the government. This picture is taken from a French engraving of 1799. The panel represents Lavoisier as he is being arrested in his laboratory by the Revolutionary Committee

AN ELEMENTARY STUDY OF CHEMISTRY

BY

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AND

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PROFESSORS OF CHEMISTRY, OHIO STATE UNIVERSITY

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PREFACE TO THE SECOND EDITION

The advance of chemistry in the last decade has made necessary the revision of this text. While thoroughly revising the subject matter the authors have made some alterations in the order of presentation. Carbon and carbon dioxide are presented at an earlier point; the chapter on neutralization is preceded by a brief chapter devoted to a metal (sodium) and a base (sodium hydroxide), and one devoted to a nonmetal (chlorine) and an acid (hydrochloric acid); the space given to the compounds of carbon has been extended a little, and the material has been brought forward into its appropriate place in the text.

In justification of this last change the authors would call attention to the fact that a very large percentage of those who take one year of chemistry do not continue the subject. It seems unreasonable that after a year of study the student should have no knowledge of the most important of the organic compounds, for he will meet with them in everyday life far oftener than with the majority of the compounds of inorganic chemistry.

The other changes incorporated in this revision are those which are suggested by the development of the science in the past ten years.

The authors wish to express their indebtedness to Mr. E. L. Mahaffey and Mr. J. H. Young for valuable assistance rendered in the revision of the text.

THE AUTHORS

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PREFACE TO THE REVISED EDITION

In offering this book to teachers of elementary chemistry the authors lay no claim to any great originality. It has been their aim to prepare a textbook constructed along lines which have become recognized as best suited to an elementary treatment of the subject. At the same time they have made a consistent effort to make the text clear in outline, simple in style and language, conservatively modern in point of view, and thoroughly teachable.

The question as to what shall be included in an elementary text on chemistry is perhaps the most perplexing one which an author must answer. While an enthusiastic chemist with a broad understanding of the science is very apt to go beyond the capacity of the elementary student, the authors of this text, after an experience of many years, cannot help believing that the tendency has been rather in the other direction. In many texts no mention at all is made of fundamental laws of chemical action because their complete presentation is quite beyond the comprehension of the student, whereas in many cases it is possible to present the essential features of these laws in a way that will be of real assistance in the understanding of the science. For example, it is a difficult matter to deduce the law of mass action in any very simple way; yet the elementary student can readily comprehend that reactions are reversible, and that the point of equilibrium depends upon rather simple conditions. The authors believe that it is worth while to present such principles in even an elementary and partial manner because they are of great assistance to the general student and because they make a foundation upon which the student who continues his studies to more advanced courses can securely build.

The authors have no apologies to make for the extent to which they have made use of the theory of electrolytic dissociation. It is inevitable that in any rapidly developing science there will be differences of opinion in regard to the value of certain theories. There can be no question, however, that the outline of the theory of dissociation here presented is in accord with the views of the very great majority of the chemists of the present time. Moreover, its introduction to the extent to which the authors have presented it simplifies rather than increases the difficulties with which the development of the principles of the science is attended.

The oxygen standard for atomic weights has been adopted throughout the text. The International Committee, to which is assigned the duty of yearly reporting a revised list of the atomic weights of the elements, has adopted this standard for their report, and there is no longer any authority for the older hydrogen standard. The authors do not believe that the adoption of the oxygen standard introduces any real difficulties in making perfectly clear the methods by which atomic weights are calculated.

The problems appended to the various chapters have been chosen with a view not only of fixing the principles developed in the text in the mind of the student but also of enabling him to answer such questions as arise in his laboratory work. They are, therefore, more or less practical in character. It is not necessary that all of them should be solved, though with few exceptions the lists are not long. The answers to the questions are not directly given in the text, as a rule, but can be inferred from the statements made. They therefore require independent thought on the part of the student.

With very few exceptions only such experiments are included in the text as cannot be easily carried out by the student. It is expected that these will be performed by the teacher at the lecture table. Directions for laboratory work by the student are published in a separate volume.

While the authors believe that the most important function of the elementary text is to develop the principles of the science, they recognize the importance of some discussion of the practical application of these principles to our everyday life. Considerable space is therefore devoted to this phase of chemistry. The teacher should supplement this discussion whenever possible by having the class visit different factories where chemical processes are employed.

Although this text is now for the first time offered to teachers of elementary chemistry, it has nevertheless been used by a number of teachers during the past three years. The present edition has been largely rewritten in the light of the criticisms offered, and we desire to express our thanks to the many teachers who have helped us in this respect, especially to Dr. William Lloyd Evans of this laboratory, a teacher of wide experience, for his continued interest and helpfulness. We also very cordially solicit correspondence with teachers who may find difficulties or inaccuracies in the text.

The authors wish to make acknowledgments for the photographs and engravings of eminent chemists from which the cuts included in the text were taken; to Messrs. Elliott and Fry, London, England, for that of Ramsay; to The Macmillan Company for those of Davy and Dalton, taken from the Century Science Series; to the L. E. Knott Apparatus Company, Boston, for that of Bunsen.

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CONTENTS

AN ELEMENTARY STUDY OF CHEMISTRY

CHAPTER I

MATTER AND ENERGY

The natural sciences. Before we advance very far in the study of nature it becomes evident that the one large study must be divided into a number of more limited ones for the convenience of the investigator as well as of the student. These more limited studies are called the *natural sciences.*

Since the study of nature is divided in this way for mere convenience and not because there is any division in nature itself, it often happens that the different sciences are very intimately related and that a thorough knowledge of any one of them requires a considerable acquaintance with several others. Thus the botanist must know something about animals as well as about plants; the student of human physiology must know something about physics as well as about the parts of the body.

Intimate relation of chemistry and physics. Physics and chemistry are two sciences related in this close way, and it is not easy to make a precise distinction between them. In a general way it may be said that they are both concerned with inanimate matter rather than with living matter, and more particularly with the changes which such matter may be made to undergo.

Changes in nature. The thoughtful observer of nature is constantly impressed by the fact that everything about him is undergoing change. All living organisms pass through a cycle of birth, development, maturity, decline, and death. Many solid rocks disintegrate rapidly when exposed to the action of the weather; with others the changes are too slow to be perceptible, but geologists have been able to show that even the most permanent rocks are gradually altered by long exposure to air and moisture. The metals we win from the ores in time rust and corrode; the structures we rear crumble; the electric current we generate is changed into the motion of the car, the light of the lamp, and the heat of the wires.

Questions suggested by the burning of fuel. Doubtless one of the changes that earliest attracted the attention of man was that which is evident during the burning of fuel. If we set fire to a piece of coal or wood, most of the solid material disappears; the ash remaining differs from the original fuel in almost every way; a flame attends the change; and both heat and light are given off.

These observations suggest a number of questions: What is the cause of these profound changes? How does the weight of the ash compare with that of the original fuel? What becomes of the material that disappears? What is the flame? What is the nature of the heat and light? Do these have weight? We shall learn many facts that partly answer these questions, but our knowledge is as yet so limited that many questions will remain but partly answered at the end of our study.

No change in weight during burning. Our ordinary experience in burning coal would lead us to suppose that a given substance loses much of its weight during burning, for the ashes of coal certainly weigh much less than the coal itself. Experiments carried out with great care show that this conclusion is too hasty. It is well known that coal will not burn unless air is present, and this fact requires explanation before we are in a position to draw conclusions about the loss of weight during combustion. If air is used up when the coal burns, it may be that other invisible gases are formed, and we shall have to know how much matter the coal loses in this way. Some experiments will throw much light upon this subject.

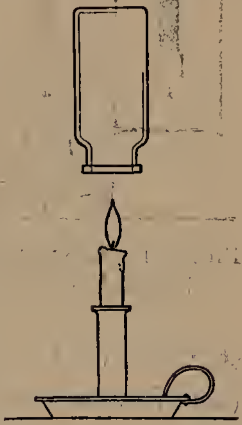


FIG. 1. Collecting the products formed from a burning candle

Experiment 1. If we pour a little clear limewater into a wide-mouthed bottle, insert a cork, and shake the bottle, we see little or no change in the liquid. If, now, we hold a similar empty bottle mouth downward over the flame of a burning candle for a few moments (Fig. 1), moisture will be seen to collect on the inside of the cold vessel, showing that water vapor is formed during burning. If we then quickly pour a few cubic centimeters of clear limewater into the bottle, insert the stopper, and shake the bottle as before, we notice that the clear liquid becomes cloudy. Some invisible gas has been formed during the burning of the candle, has risen into the bottle, and has produced a change in the clear limewater. This gas is called carbon dioxide.

Experiment 2. The conclusion we have reached may be confirmed by a second experiment. A candle *A* (Fig. 2) is arranged on one pan of a large balance and over it is suspended a lamp chimney or cylinder (*B*) open at both ends and closely filled with pieces of soda lime (a solid substance that absorbs both water vapor and carbon dioxide). The candle and cylinder are then balanced by the weights *C*. As the candle burns, the pan on which it rests *sinks*, showing that the weight of the products formed by the burning of the candle and absorbed by the soda lime is greater than the weight of the portion of the candle burned.

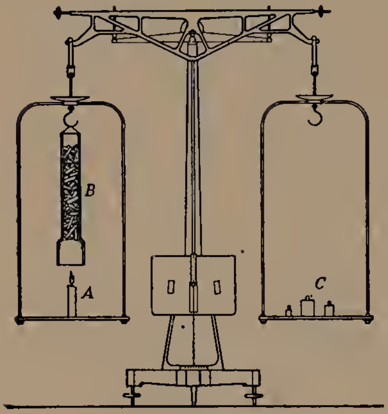


FIG. 2. Demonstration of increase in weight during burning

The experiments of Lavoisier. Long before he begins the study of chemistry every student learns that the air contains an invisible gas called oxygen. Soon after the discovery of oxygen as a constituent of the air the great French chemist, Lavoisier (see frontispiece), made some experiments that enabled him to determine the changes taking place when a substance burns, or, as it is often expressed, when a substance undergoes combustion. He placed some pieces of solid materials (tin, iron, phosphorus) in a flask full of air, closed the flask, and weighed the whole. He then heated the flask and its contents until combustion took place, noting that not all of the solid had burned. When the burning had ceased he cooled the flask and weighed the whole once more and found that there had been no change in weight as the result of combustion, although both heat and light had been evolved, and heat had been applied to the flask.

On opening the flask, air rushed in, showing that the solid in burning had absorbed the air; but the volume of air that entered was much less than the volume originally present, proving that not all of the air had been absorbed during combustion. The flask was again weighed, the increase in weight being the weight of the air that had entered the flask. The solids, including the products of combustion and the unburned materials, were then weighed, and the weight was found to be greater than before combustion. *The gain in weight was found to be exactly equal to the weight of the air used in the burning.* By other experiments Lavoisier was able to show that when a substance burns in air, not all the constituents of the air are used up, but only the oxygen present.

Results of the experiments. These experiments proved many important facts — among them that the act of combustion depends upon the oxygen of the air as well as upon the material undergoing combustion; that the total weight of the materials concerned is not changed during combustion; and that the light and heat given off during combustion occasion no loss of weight, so these can have no weight.

Matter and energy. As the result of much experience we have come to recognize that in all changes similar to combustion there are two fundamentally different things concerned: (1) the material that possesses weight or mass and which we call *matter*; (2) the light and heat given off, which have no weight and which we call *energy.* We shall now examine these two somewhat more closely.

Forms of energy. We sometimes say of a man that he is full of energy, meaning that he has a great capacity for work. Indeed energy is often defined as capacity for work, or ability to do work, although no simple definition as yet proposed is entirely satisfactory. We recognize this same capacity for work in inanimate things. Steam, highly compressed in a boiler, possesses energy, for on being admitted to the cylinder of a locomotive it will push back the piston and thus move the train. Energy is present in electrical power lines, for through the necessary mechanical devices we can obtain power, heat, and light from this source. A moving body possesses kinetic energy, and if the body is suddenly stopped, this energy appears as heat.

Conservation of energy. The experience gained in a century of experimenting has convinced scientists that it is impossible to alter the quantity of energy in a system of bodies, save as we add energy from without or allow it to escape from the system, and this generalization is known as the *law of the conservation of energy.* It is not difficult, however, to transfer energy from one body to another. If a piece of hot metal is dipped into water, the metal is cooled and the water is heated, so that the metal loses energy and the water gains it. When a swinging bat strikes the ball, the ball gains energy while the bat loses it. It is evident, therefore, that a given body does not possess a constant quantity of energy as it possesses constant mass.

Transformation of energy. Moreover, energy can be freely transformed from one kind into another. The heat energy of burning coal can be changed into the kinetic energy of the locomotive. The kinetic energy of falling water can be transformed into electrical energy, as in the power plants of Niagara Falls. The electrical energy of the trolley line is readily converted into the kinetic energy of the moving car. In all such transformations a definite quantity of energy of one kind always gives a definite quantity of another, so that we speak of the mechanical equivalent of heat, or of the electrical equivalent of mechanical energy.

The diagram (Fig. 3) illustrates a few familiar transformations of energy. The heat of the flame *A* is converted into mechanical energy in the heat engine *B*. The motion of the engine is communicated to the small dynamo *C*, where it is converted into magnetic and electrical energy. The electrical energy is changed into heat and light in the incandescent lamp *D*, and into chemical energy (see following paragraph) by the decomposition of water in *E*.

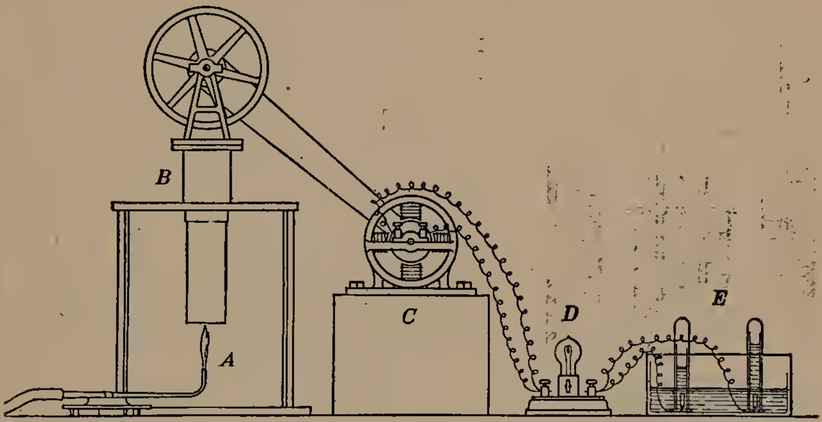


Fig. 3. Diagram illustrating some transformations of energy

Chemical energy. A body may possess energy due to its motion or to its position. A piece of coal, however, possesses energy due neither to its motion nor to its position but to its ability to undergo combustion, for in this process both heat and light are evolved. Our experience teaches us to believe that this heat and light must have come from some other form of energy present in the coal and the oxygen which unite in the process of burning. This form of energy is called *chemical energy.* It is the form possessed by substances which enables them to undergo changes similar to combustion, and it is the form of energy in which the chemist is especially interested.

The measurement of energy. Since changes in energy are so constantly taking place all about us, it is a matter of great practical importance to devise units for the measurement of energy, and methods for making the measurement. In general, each kind of energy must have its own units of measurement, just as with matter we have centimeters for lengths, liters for volumes, and grams for weights. In some of its forms energy is very difficult to measure directly, and neither units nor methods for the direct measurement of chemical energy have as yet been devised. In such cases it is necessary to transform the energy into a form more convenient for measurement. In the case of chemical energy it is changed into heat or electrical energy for this purpose.

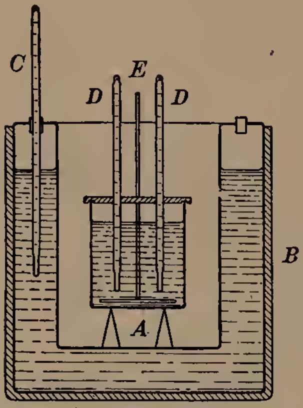


Fig. 4. A calorimeter

Measurement of heat. A quantity of heat energy is measured by observing to what extent it will change the temperature of a given mass of some standard substance. Water has been chosen as the standard, and the unit of heat is called the *calorie* (designated by the abbreviation *cal.*). It is defined as *the quantity of heat required to change the temperature of one gram of water one degree on the centigrade scale.*

The actual measurement of the quantity of chemical energy transformed into heat in any definite change is accomplished by the use of an apparatus called the *calorimeter*, represented in Fig. 4. The change is arranged to take place in solution in a measured volume of water contained in a thin-walled metal vessel *A*. This is placed within a double-walled vessel *B*, which contains water at the temperature of the room. The thermometer *C* indicates when the water has reached this temperature. This water is to prevent the influence of heat from without, and as an added precaution the vessel is covered with a thick layer of nonconducting felt. The heat evolved by the change raises the temperature of the solution, the rise being indicated by the thermometers *D*, *D*. During the change the solution is stirred by the stirrer *E*. If the weight of the water is (say) 2570 grams and the rise in temperature is 1.5° centigrade, the heat evolved is $2570 \times 1.5 = 3855$ cal.

Matter and its properties. By *matter* we mean anything that possesses weight, or mass. When a material object is at rest it takes an expenditure of energy to set it in motion, and we express this fact by saying that matter possesses *inertia*. Similarly, when a body is in motion it requires an expenditure of energy to stop it, or to overcome its inertia. By the term *property* we mean a mark or characteristic by which we identify a given thing. Each form of matter has many properties peculiar to itself, such as its physical state (solid, liquid, or gas), its hardness, density, luster, and shape; but *mass* and *inertia* are the two characteristics or properties that all kinds of matter have in common.

Law of conservation of matter. Like energy, matter may oftentimes be changed from one form into another; thus we have seen that the solid candle burns away, giving rise to invisible gases. The solid ice is easily changed into liquid water and gaseous steam. The question naturally arises whether there is any increase or decrease in the weight of the matter as a result of these changes. Much careful experimenting has shown that there is not. The weight of the products formed in any change in matter always equals the weight of the substances undergoing change.

We may alter the form of matter but not its mass. This important truth, known as the *law of the conservation of matter*, may be stated thus: In any changes to which we may subject a given quantity of matter, the mass remains unchanged.

Units used and their abbreviations. In the chapters to follow, all temperature readings given will be those of the centigrade scale, unless otherwise designated. In referring to other units of measurements, the commonly accepted abbreviations will be employed, such as g. for gram, kg. for kilogram, cc. for cubic centimeter, l. for liter, and lb. for pound.

EXERCISES

1. Give instances of the overlapping of different sciences, taken from your own experiences in the study of these sciences.

2. Point out the fundamental difference in the changes involved in (*a*) the crushing of a stone and (*b*) the burning of a piece of coal.

3. How do the ashes of coal compare in weight with the original coal? Why do some coals, when burned, leave more ashes than others?

4. How do you account for the fact that when a lamp is lighted, a film of moisture is deposited on the chimney? Is the film deposited on the inside or the outside of the chimney? Why does the film soon disappear?

5. Suggest the reason why moisture often collects on windows of rooms heated by gas stoves or grates.

6. Narrate some of the important incidents in the life of Lavoisier (consult encyclopedia).

7. Give instances illustrating the law of the conservation of energy, and the law of the conservation of matter.

8. The energy of the falling water at Niagara Falls is utilized in propelling, heating, and lighting the trolley cars at Buffalo. Trace the changes of energy involved.

9. What is the source of the energy of the body?

10. Why does the body become warm with exercise?

11. Trace the energy changes between the coal on the locomotive and the sound of the whistle that one hears.

12. In Experiment 1, why does the water vapor change into visible moisture on the sides of the bottle?

13. How many forms of energy can you name?

14. How would you define the term *mechanical equivalent of heat*?

15. The fuel value of a coal was determined by burning 1 g. of the coal in a calorimeter containing 2500 g. of water. The heat liberated raised the temperature of the water 1.5°. Calculate the number of calories of heat evolved by the burning of the coal.

16. A certain fuel gives out 4000 cal. per gram when burned. What weight of it would be required to heat 3 l. of water from room temperature (18°) to the boiling point, supposing that all the heat evolved is used in raising the temperature of the water?

CHAPTER II

VARIETIES OF MATTER: COMPOUNDS, ELEMENTS, MIXTURES

Varieties of matter. The variety of forms which matter assumes in all the wonderful transformations of nature is almost infinite, and these forms may be classified in a great many ways, according to the purpose in view. The interest of the chemist centers chiefly in the composition of substances and in their chemical energy, together with the changes which take place in both of these. From this standpoint he finds it convenient to arrange matter in three groups; namely, *compounds*, *elements*, and *mixtures*.

Illustrative experiments. The distinction between these three classes can be explained best by the following illustrative experiments.

Experiment 1. The chief properties of the substances iron and sulfur are familiar to almost everyone. Iron filings form a heavy gray powder, strongly attracted by the magnet. When treated with the liquid known as hydrochloric acid, the iron passes into solution and a colorless gas called hydrogen is evolved, considerable heat being liberated in the process. Sulfur may be obtained as a light yellow powder not attracted by a magnet nor dissolved by hydrochloric acid. It is readily soluble in the liquid known as carbon disulfide, however, while iron is not soluble, and when the solution is allowed to evaporate, the sulfur is deposited in the form of yellow crystals.

When iron filings and sulfur are thoroughly ground together, a greenish-black powder is obtained which in appearance is quite different from either of them; but when we apply the tests which we have found to characterize iron and sulfur, it is found that in many respects the powder acts like these two taken separately. Hydrochloric acid still dissolves the iron and evolves hydrogen with the same heat as before, leaving the sulfur unchanged. A magnet rubbed through the material withdraws the iron and leaves the sulfur. Carbon disulfide dissolves the sulfur but not the iron. The sulfur and the iron each act just as they did before they were ground together, and with the same energy.

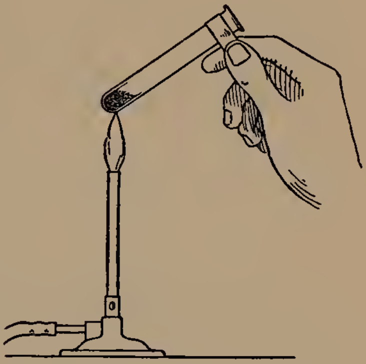


Fig. 5. Heating a mixture of iron and sulfur

If, now, a portion of the powder is placed in a test tube and heated, as shown in Fig. 5, it soon begins to glow at the point of greatest heat, and even if the flame is withdrawn, the glow continues to spread throughout the entire contents of the test tube, and a great deal of heat is set free at the same time. When the product is examined, it is found that many of the characteristics of the iron and sulfur have been modified. Carbon disulfide no longer dissolves sulfur and leaves iron; a magnet has no effect upon the material; hydrochloric acid dissolves the entire product and evolves a gas of disagreeable odor quite different from hydrogen; and the heat liberated is quite different in quantity from that in the former case. The new product also differs from the iron and the sulfur in density, color, hardness, solubility, and melting point.

The product which is formed by the union of iron and sulfur is called iron sulfide.

Experiment 2. When a small quantity of sugar is heated in a test tube, it melts, turns brown in color, gives off vapors, and finally dries up to a solid black residue which may be identified as carbon. By collecting and examining the vapors it is possible to show that they are largely water. To make this transformation complete it is necessary to apply heat throughout the entire process. In this experiment one substance, merely by the application of heat, has given rise to two others of very different properties, and the change is described as a *decomposition.*

Chemical reactions. The two experiments that have just been described are very different in many ways, but they have several characteristics in common. Most of the properties of the materials concerned undergo a very considerable change, so that the products formed are different from the original materials. A more important characteristic is that the chemical energy of the materials has been changed. The action of iron with sulfur, when once started, is attended by the evolution of a great deal of heat, and this is at the expense of the chemical energy of the original substances. To effect the decomposition of sugar it is necessary to supply heat during the entire period of decomposition, and this heat must be converted into some other form of energy. A part of it is converted into chemical energy, so that the carbon and the water taken together represent more energy of this kind than does the original sugar. Any change in the composition of matter, whether union or decomposition, that involves a change in the chemical energy of the substances concerned is called a *chemical action* or a *chemical reaction.*

Definition of chemical compounds. When it can be shown that a substance is composed of at least two different materials, and that its chemical energy is different from that of the constituents taken separately, it is called a *chemical compound.* Thus, we judge iron sulfide to be a chemical compound, for it contains iron and sulfur, and yet differs from them in chemical energy. It is not always a simple matter to determine whether a given material is a chemical compound or not. We are assisted in our decision by the fact, to be proved in a later chapter, that the percentage composition of a given compound is always the same. Thus, iron sulfide always contains 63.52 per cent iron and 36.48 per cent sulfur. If the material can be obtained in pure form and analyzed, it is usually possible to decide whether or not it is a compound by the constancy of its composition.

Chemical affinity. It is important to distinguish clearly between chemical action and the force that brings about the action. This force is called *chemical affinity.* For example, we say that iron and sulfur combine because of their chemical affinity. We can form little idea, as yet, as to the nature of this force, just as we have little idea as to the nature of the force of gravitation. In both cases we merely give names to forces which we must believe to be acting.

Conditions affecting chemical action. There are many conditions which may either promote or hinder chemical action. An increase in temperature is usually favorable to chemical action, as was seen in the case of iron and sulfur. It frequently promotes decomposition, as in the case of sugar. Other forms of energy, such as light, mechanical pressure, shock, and electrical energy, may also facilitate either chemical union or decomposition, at times overcoming obstacles which prevent union, in other cases overpowering the chemical affinity which holds a compound together.

Chemical conduct of substances. Substances differ very greatly from each other in the way in which they act toward other substances. Thus, a substance may burn with a flame when heated in the air, or it may combine with another substance with incandescence, as is the case of iron heated with sulfur. It may decompose when heated, as is true of sugar, or when subjected to the action of the electric current, as water does. All such peculiarities are collectively called the *chemical conduct* of a substance.

Elements. We have seen that sugar can be decomposed into two different substances, namely, water and carbon. The question naturally arises whether or not the water and carbon, as well as other forms of matter, such as iron and sulfur, can likewise be decomposed into other substances. To determine whether or not any given substance can be decomposed, we may heat the substance, as in the case of sugar; or we may employ other agencies. For example, experience has shown that in many cases decomposition may be brought about by the electrical current or by the action of substances possessed of great chemical energy, and we may also employ these methods. In such ways chemists have succeeded in decomposing water into two invisible gases, oxygen and hydrogen, so that water must be regarded as a compound.

The decomposition of water. The decomposition of water may readily be observed by the aid of an apparatus such as that represented in Fig. 6. Two test tubes, *A* and *B*, are filled with water and inverted in a vessel half filled with water to which a little sulfuric acid has been added. A piece of platinum foil, *C* and *D*, attached to a wire is then brought under the end of each tube. When these wires are connected with a source of current supplying from 6 to 10 volts, bubbles of gas will be seen to form in each tube. These gases may be shown to have different properties; they are hydrogen and oxygen. The reason for adding the sulfuric acid will be discussed later.

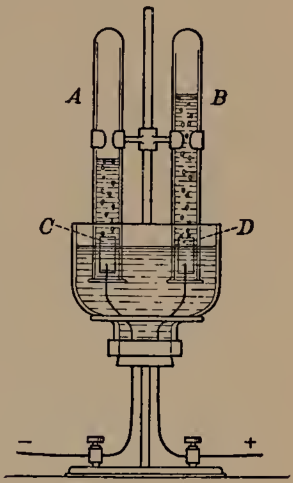


FIG. 6. The decomposition of water into oxygen and hydrogen by the electric current

On the other hand, carbon, iron, and sulfur have never been decomposed, notwithstanding the many efforts directed to this end. Substances like these three, which have never been decomposed into two or more different materials, are called *elements*, or *elementary substances*. It should be carefully noted, however, that this definition does not suggest anything as to the real nature of an element. Neither does it preclude the possibility that one element may be transformed into another under some condition which changes its chemical energy. In the discussion of radium it will be shown that this element is slowly changing into others.

Number of the elements. While many thousands of compounds have been described, the number of the elements at present known is comparatively small. A complete list is given in the table on the inside back cover of this book. Following the name of each element in the table is an abbreviation called a *symbol*, by which the element is designated among chemists. The symbol is usually the initial letter of the name of the element, together with some other characteristic letter. In the case of some of the elements the symbol is the abbreviation of the old Latin name, as is true of iron (*ferrum*), gold (*aurum*), and mercury (*hydrargyrum*). The significance of the column of numbers will be made clear a little later.

Physical state of the elements. About ten of the elements are gases at ordinary temperatures. Two — mercury and bromine — are liquids. The others are all solids, though their melting points vary through wide limits, from cæsium, which melts at 26°, to elements which do not melt save in the intense heat of the electric furnace.

Occurrence of the elements. Comparatively few of the elements occur as uncombined substances in nature, most of them being found in the form of chemical compounds. When an element does occur by itself, as is the case with gold, we say that it occurs in the *free state*, or *native*; when it is combined with other substances in the form of compounds, we say that it occurs in the *combined state*, or in *combination*. In the latter case there is usually little about the compound to suggest that the element is present in it; for we have seen that elements lose their own peculiar properties when they enter into combination with other elements. From its appearance it would never be suspected that the reddish, earthy-looking iron ore contains iron.

Names of the elements. The names given to the elements have been selected in a great many different ways. (1) Some names are very old and their original meaning is obscure. Such names are *iron*, *gold*, and *copper*. (2) Many names indicate some striking physical property of the element. The name *bromine*, for example, is derived from a Greek word meaning "stench," referring to the extremely unpleasant odor of the substance. (3) Some names indicate the chemical conduct of the elements. Thus, *nitrogen* means "the producer of niter," nitrogen being a constituent of niter, or saltpeter; *argon* means "lazy, or inert," the element being so named because of its inactivity. (4) Other elements, as germanium and strontium, are named from countries or localities. (5) Still others, as tantalum, suggest characters in mythology.

Distribution of the elements. So far as we can judge, these elements are of very unequal occurrence in nature. It must be remembered, however, that our knowledge of the earth's composition is confined to what is a comparatively thin surface shell, not exceeding a few miles in thickness. The table below, prepared by F. W. Clarke and based on the analysis of representative rocks and minerals, gives an estimate of the composition of this solid shell. It will be seen that nine of the elements are estimated to constitute 98.4 per cent of the shell. Some of the elements are of such rare occurrence that only a few grams have ever been isolated.

COMPOSITION OF THE EARTH'S CRUST

Oxygen	47.07%	Potassium	2.45%
Silicon	28.06%	Sodium	2.43%
Aluminium	7.90%	Magnesium	2.40%
Iron	4.43%	Hydrogen	0.22%
Calcium	3.44%	Other elements	1.60%

Elements essential to life. A careful examination of the materials present in living organisms shows that only a few are of vital importance to us. The following table, compiled by Sherman, indicates the average composition of the human body. It is possible that other elements have an importance which we do not realize, but, so far as we can judge, these are the only ones upon which living organisms are dependent.

AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen	65.00%	Phosphorus	1.00%	Magnesium	0.05%
Carbon	18.00%	Potassium	0.35%	Iron	0.004%
Hydrogen	10.00%	Sulfur	0.25%	Iodine	traces
Nitrogen	3.00%	Sodium	0.15%	Fluorine	traces
Calcium	2.00%	Chlorine	0.15%	Silicon	traces

Mixtures. It is quite possible to prepare, either from elements or from compounds, or from both, a body which is not itself a compound but is merely a mixture. Ordinary concrete is such a material, for in a broken piece it is easy to identify the crushed stone, the sand, and the cement which compose it. Granite is a sort of natural concrete, in which two very different-looking crystalline materials, mica and feldspar, are bound together by a glassy substance called silica. Iron and sulfur when rubbed together form a material more closely resembling a compound, in that it is apparently of even quality throughout, or is *homogeneous.* An examination under the microscope shows that this is not really so, for the particles of iron and sulfur can still be seen lying side by side unchanged.

Alchemy. In olden times it was thought that some way could be found to change one element into another, and a great many efforts were made to accomplish this transformation. Most of these efforts were directed toward changing the commoner metals into gold, and many fanciful ways for doing this were described. The chemists of that time were called *alchemists,* and the art which they practiced was called *alchemy.* The alchemists gradually became convinced that the only way common metals could be changed into gold was by the wonderful power of a magic substance which they called the *philosophers' stone,* which would accomplish this transformation by its mere touch and would in addition give perpetual youth to its fortunate possessor. No one has ever found such a stone, and no one has succeeded in changing one metal into another.

One of the most brilliant discoveries of recent years seems in one sense to come near realizing the dreams of the alchemists, for it has been shown that one or two undoubted elements are very slowly changing into others. But no one has been successful in either hastening or retarding the change.

FIG. 7. An alchemist's laboratory, according to the painting of Teniers

The domain of chemistry. With the general characteristics of matter and energy before us, it is now possible for us to form some idea of the topics that are of fundamental interest to the chemist. In the first place, the chemist is concerned with the composition of matter. For example, such questions as whether a given substance is an element or a compound; how it may be obtained in pure form and what its properties and uses are;

whether a certain rock contains iron or gold; whether a given sample of drinking water contains anything that is injurious to health, — these are questions for the chemist to decide. Moreover, the chemist is equally interested in the changes both in form and energy which any given substance undergoes. It is of fundamental importance that he should know what compounds any given element will form; what the nature of these compounds is; which of two given samples of coal evolves the greater amount of heat on burning; and what the function of the various classes of foods is and what mixture of these is best adapted to preserve health under different physical conditions. It is with questions of this kind that we shall be concerned in the study of chemistry.

EXERCISES

1. What means of decomposing a compound can you suggest besides heating?

2. Define a compound; an element. Which group is the more numerous?

3. What is meant by the earth's crust?

4. Does the fact that a substance undergoes no change on heating show it to be an element?

5. Read over the list of elements. What ones do you know to occur native?

6. Aluminium is much more abundant than iron (see Clarke's table). How do you account for the much greater cheapness of iron?

7. Consult the dictionary for the derivation and significance of the names of the following elements: phosphorus, hydrogen, germanium, columbium, chlorine, argon, copper, selenium, thorium, iodine.

8. Give examples of chemical action caused through the agency of heat; of light; of electricity.

9. Calculate the approximate weights of the principal elements present in your body.

10. How do you account for the fact that the mound builders used vessels of copper rather than of iron?

11. Give reasons why gold is more costly than iron.

12. Give reasons why iron does not occur native to any extent.

13. What is a characteristic property of all the elements that occur native?

14. What is meant by the physical state of an element?

15. Would the fact that iron is present in the human body in such very small amounts suggest that we could get along without it?

16. Why is the list of elements subject to change from year to year?

17. What can you add to what has been said about the alchemists? (Consult Encyclopedia.)

CHAPTER III

OXYGEN

Historical. The discovery of oxygen is attributed to the English chemist Priestley, who in 1774 obtained the element by heating a compound of mercury and oxygen now known as red oxide of mercury. It is probable, however, that other investigators, especially the Swedish chemist Scheele, had obtained it at an earlier date but failed to attract attention to their discovery. The name *oxygen* signifies "acid former." It was given to the element by the French chemist Lavoisier, since he believed that all acids owe their characteristic properties to the presence of oxygen. This idea we now know to be incorrect.

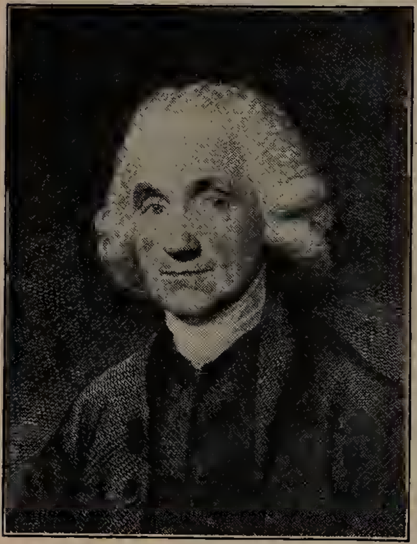


FIG. 8. Joseph Priestley (1733–1804)

The discoverer of oxygen

Occurrence. Oxygen is by far the most abundant of all the elements. It occurs both in the free state and in combination. In the free state it is found in the air, 100 volumes of *dry* air containing about 21 volumes of oxygen. In the combined state it forms 88.81 per cent of water and nearly one half of the rocks composing the earth's crust. It is also an important constituent of the compounds that compose plant and animal tissues; for example, about two thirds, by weight, of the human body is oxygen.

Preparation. While oxygen is very abundant, it does not occur in nature in pure condition. To obtain pure oxygen we must either liberate it from some compound or separate it from the gases with which it is mixed in the air. The most important of the methods for preparing the pure element are the following:

1. *Preparation from water.* Water is a compound, consisting of 88.81 per cent oxygen and 11.19 per cent hydrogen. It is easily separated into these constituents by passing an electric current through it, as has been already explained (pp. 16, 17).

2. *Preparation by heating certain compounds of oxygen.* Some of the compounds of oxygen, when heated, give off at least a portion of their oxygen. For example, mercuric oxide, a solid compound containing 7.39 per cent of oxygen and 92.61 per cent of mercury, is decomposed into its elements by heating it. The change may be represented in the following way, in which the names of the elements composing the compound are inclosed in brackets just beneath the names of the compounds:

$$\underset{\begin{bmatrix}\text{mercury}\\ \text{oxygen}\end{bmatrix}}{\text{mercuric oxide}} \longrightarrow \text{mercury} + \text{oxygen}$$

The compound best adapted for the preparation of oxygen by this method is potassium chlorate. This compound is a white solid containing 39.16 per cent of oxygen, 31.90 per cent of potassium, and 28.94 per cent of chlorine. When heated it undergoes a series of changes in which all the oxygen is finally set free, leaving a white solid compound of potassium and chlorine called potassium chloride. The change may be represented as follows:

$$\begin{array}{lcl} \text{potassium chlorate} & \longrightarrow & \text{potassium chloride} + \text{oxygen} \\ \left[\begin{array}{l}\text{potassium}\\ \text{chlorine}\\ \text{oxygen}\end{array}\right] & & \left[\begin{array}{l}\text{potassium}\\ \text{chlorine}\end{array}\right] \end{array}$$

The evolution of the gas becomes marked at about 400°. It is a remarkable fact that the rate at which the oxygen is evolved at any given temperature is greatly increased by the presence of small quantities of certain substances, notably manganese dioxide. By mixing such a substance with the chlorate it is possible, therefore, to obtain the oxygen rapidly at a lower temperature than would otherwise have to be employed. As to the way in which the manganese dioxide promotes the decomposition, it may be said at once that we do not know. Apparently it undergoes no change during the reaction. Certainly it contributes no oxygen, for the weight of oxygen obtained is always 39.16 per cent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. This is but one example of many in which the rate of change is influenced by an apparently inactive substance. Such materials are called *catalytic agents*, or *catalyzers*, and we shall meet with them frequently in subsequent pages, since a great many chemical processes depend upon suitable catalyzers for their success.

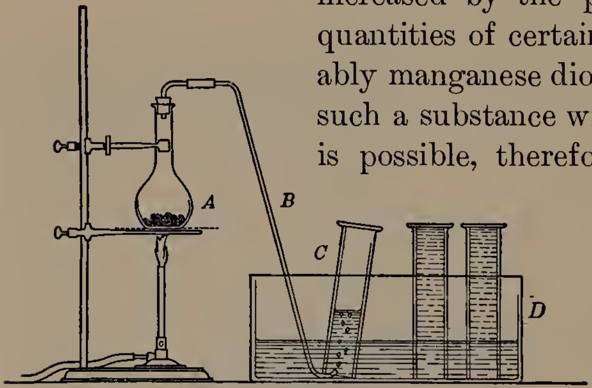


FIG. 9. Preparation of oxygen from potassium chlorate, and method of collecting the gas

Laboratory preparation of oxygen. The preparation of oxygen from potassium chlorate as commonly carried out in the laboratory is as follows:

The potassium chlorate, mixed with about one fourth of its weight of manganese dioxide, is placed in a suitable vessel, such as a glass flask, which is provided with a stopper and glass tube, as shown in *A* (Fig. 9). Upon applying a gentle heat, oxygen is evolved and passes out through the tube *B*. It is evident that the oxygen which first escapes is mixed with the air contained in the flask. In a short time, as the evolution of oxygen continues, all this air is displaced, and the pure oxygen may then be collected by bringing the end of the delivery tube under the mouth of a glass cylinder *C*, which has been filled with water and inverted in a trough of water *D*, as shown in the figure. The gas rises in the cylinder and displaces the water. In preparing larger quantities of oxygen a copper retort (Fig. 10) having a capacity of from 500 to 1000 cc. may be used to advantage in place of the more fragile glass flask.

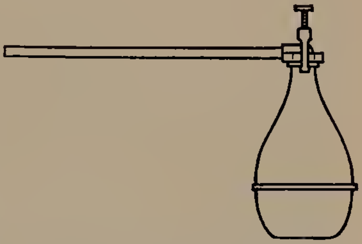


FIG. 10. Copper retort for making oxygen

3. ***Preparation from sodium peroxide.*** This compound is a white solid containing 41.02 per cent of oxygen. When water is brought into contact with it, the two react in such a way as to liberate a portion of the oxygen. This reaction may be expressed as follows:

$$\underset{\begin{bmatrix}\text{sodium}\\ \text{oxygen}\end{bmatrix}}{\text{sodium peroxide}} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} \longrightarrow \underset{\begin{bmatrix}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{sodium hydroxide}} + \text{oxygen}$$

While this is an expensive method, it is often used because of its simplicity. It is only necessary to bring the two compounds together in order to obtain the gas.

4. ***Preparation from air.*** Since air contains such a large percentage of free oxygen, one would naturally expect methods to be devised for obtaining oxygen from this source. The problem is not so simple as it may seem, for there are other gases in the air, and the separation of a gas in pure condition from a mixture of gases is always difficult.

To accomplish the separation, the air is first subjected to the combined effects of pressure and low temperature. In this way it is possible to obtain it in the form of a liquid which is essentially a mixture of oxygen and nitrogen in the liquid state. When this liquid is allowed to stand under ordinary pressure, it boils rapidly and its temperature falls to a very low point. Since nitrogen has the lower boiling point (−195.7°), it tends to boil away first, and is gradually followed by the oxygen (boiling point, −182.9°), which may be collected separately.

Laboratory and commercial methods of preparation. We have seen that a number of different methods may be used for the preparation of oxygen. We shall find as we proceed that this is true in reference to most of the other elements. Some of these methods are expensive, while others necessitate the use of complicated apparatus or costly machinery. For the purpose of laboratory experiments, in which relatively small quantities are desired, the choice of the method will naturally be decided by convenience and simplicity of apparatus, while in the preparation on a commercial scale economy will determine the method. In the case of oxygen the method of preparation from potassium chlorate has proved itself the most suitable for laboratory purposes. For commercial purposes oxygen is obtained either from water (method 1) or from air (method 4).

Properties of oxygen. Oxygen is a colorless, odorless, tasteless gas, slightly heavier than air. One liter of it, measured at a temperature of 0° and under a pressure of 1 atmosphere, weighs 1.4290 g., while under similar conditions 1 l. of air weighs 1.2928 g. It is but slightly soluble in water, 100 volumes of water at 0° and under ordinary atmospheric pressure dissolving about 4 volumes of the gas. Oxygen, like other gases, may be liquefied by applying very great pressure to the highly cooled gas. When the pressure is removed, the liquid oxygen passes again into the gaseous state, since its boiling point under ordinary atmospheric pressure is −182.9°. By reducing the temperature still lower oxygen is obtained in the form of a snowlike solid which melts at −235°. For purposes of transportation the gas is pumped under great pressure into strong steel cylinders (Fig. 11), and it may be purchased in this form.

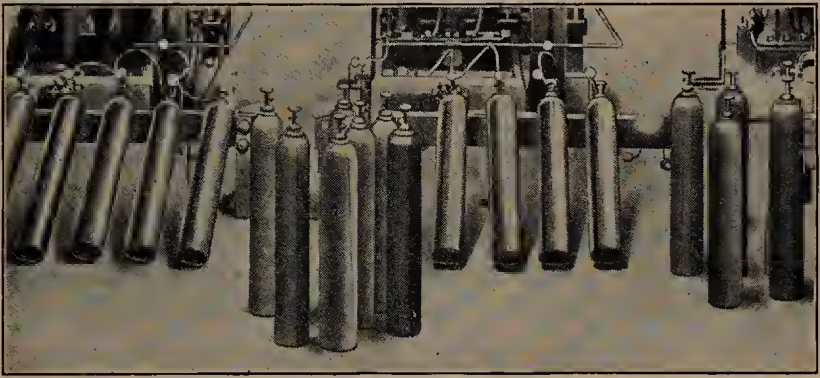


Fig. 11. Oxygen stored in steel cylinders

Chemical conduct. At ordinary temperatures oxygen is not very active; most substances either are not affected by it or are affected so slowly that the action escapes notice. At higher temperatures, however, oxygen is very active and unites directly with most of the elements. This may be shown by heating various substances until they are just ignited in air, and then bringing them into vessels containing oxygen, when they burn with greatly increased brilliancy. Thus, a glowing splint introduced into a jar of oxygen bursts into flame. Sulfur burns in air with a very weak flame and a feeble light; in oxygen the flame is increased in size and brightness (Fig. 12). Substances which burn readily in the air, such as phosphorus, burn in oxygen with dazzling brilliancy. Many substances which burn in the air with great difficulty, such as iron, burn readily in oxygen.

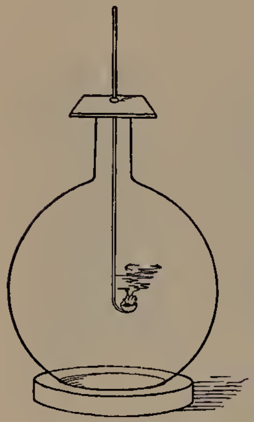


FIG. 12. Burning sulfur in oxygen

The nature of the action of oxygen upon substances; oxidation; oxidizing agent. It is possible to show by experiment that the action of oxygen upon another element consists in the union of the two elements to form a compound. Thus, when sulfur burns in oxygen, both sulfur and oxygen disappear as such, and in their place we find a gaseous compound composed of the two elements. Likewise, when phosphorus or iron or carbon burn in oxygen, compounds of these elements with oxygen are formed. Many compounds as well as elements burn readily both in air and in oxygen; among these are coal, wood, oil, and gas. In the majority of such cases the compound is completely decomposed and each of its constituent elements combines with oxygen. Thus, most oils are made up of carbon and hydrogen, and when the oil burns it is converted into a compound of carbon and oxygen (carbon dioxide) and a compound of hydrogen and oxygen (water). Less frequently the compound undergoes no decomposition but merely as a whole combines with oxygen.

The general term *oxidation* is applied to all such processes as those described above, in which any substance or its constituent parts combines with oxygen. Thus, we speak of the oxidation of phosphorus or sulfur by the air or by pure oxygen, and we say that these elements readily undergo oxidation. The material which supplies the oxygen is called the *oxidizing agent*. In the examples just mentioned the air or pure oxygen is the oxidizing agent, but in many cases the oxygen is supplied by some compound such as potassium chlorate or sodium peroxide.

Oxides; products of oxidation. When any element combines with oxygen, the resulting compound is known as an *oxide* of that element. Thus, the compound formed by the union of sulfur with oxygen is known as an oxide of sulfur. Likewise, when phosphorus or iron or carbon combine with oxygen, the resulting compounds formed are oxides. The particular oxide or oxides formed in the oxidation of any substance are known in general as the *products of oxidation* of that substance.

Oxides of nearly all the elements have been prepared, and they constitute an important class of compounds. Some of these oxides are invisible gases, as is true of the oxides of sulfur and of carbon. In a few cases the oxide is a liquid, the most familiar example being water, which is an oxide of hydrogen. In the great majority of cases, however, the oxides are solids, which is true of those of iron and phosphorus. It is easy to understand, therefore, why such elements as sulfur and carbon completely vanish on burning, leaving no ash, while other elements, such as iron and phosphorus, leave a solid residue.

Combustion. Sometimes oxidation takes place so slowly that no light is seen and, unless careful measurements are made, no heat is noticed. The decay of vegetable matter, such as wood and leaves, is an example of this slow oxidation. In other cases, as with burning phosphorus or iron, light is given off either as a flame or as a glow called *incandescence.* In such cases the substance is said to undergo *combustion.* In its broad sense the term *combustion* is applied to any chemical reaction in which light is evolved. The most familiar examples of combustion are those in which substances burn in air or oxygen, and which are therefore also oxidations. Ordinarily, when we speak of a combustible substance we mean one that will burn in air or oxygen.

Heat of oxidation and combustion. Evidently a given substance may either undergo a slow oxidation or it may undergo combustion. Thus, a piece of phosphorus, exposed to the air in a cold room, slowly wastes away until it has all disappeared into smoke consisting of an oxide of phosphorus; but if it is touched with a lighted match, it takes fire and burns very rapidly, giving out much heat in its combustion. The product is the same in both cases; namely, an oxide of phosphorus. Apparently the difference lies in the amount of heat given off, but very accurate experiments demonstrate that this, too, *is exactly the same.* In the one case the action is so slow that the heat is conducted away as fast as it is liberated, and so it escapes notice; in the other it is given off so rapidly as to be very striking. A similar relation has been found to hold true in all cases of combustion. The heat given off when a definite weight of a substance undergoes oxidation is exactly the same whether the action is fast or slow, *provided the same compound is formed.*

Spontaneous combustion. It has been found that the rate at which oxidation goes on is greatly increased by raising the temperature of the material undergoing oxidation. Consequently, if the conditions surrounding oxidation are such that the heat given off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature, until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature.* Materials taking fire in this way are said to undergo *spontaneous combustion.* It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation. Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm dry place. Sometimes the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or barn if the hay is not well dried before being stored.

Importance of oxygen. The great importance of oxygen in nature is evident from the facts which have already been presented in this chapter. It is a constituent of the great majority of the compounds which collectively constitute the solid earth, the living creatures upon it, and the water which covers so much of its surface, while the atmosphere is a great reservoir from which a supply of the free element can be drawn at any time.

Free oxygen is essential to the life of all organisms, with the exception of some of the lowest forms. Aquatic animals obtain the necessary oxygen from the air dissolved in the water in which they live. Free oxygen also plays a prominent part in the decomposition of refuse organic matter, much of it being oxidized into harmless gases (Fig. 13). It is noteworthy, however, that the oxidation of such matter takes place only in the presence of certain minute forms of living organisms known as bacteria.

Free oxygen is also utilized in a great variety of industrial processes, but for most of these, air answers every purpose, since the nitrogen which it contains does not seriously interfere. Pure oxygen finds application in quite a variety of scientific experiments, in the production of very high temperatures, and in the treatment of certain diseases in which the patient is unable to inhale sufficient air to supply the necessary quantity of oxygen.

Fig. 13. Sewage-disposal plant at Columbus, Ohio, in which the sewage is sprayed into the air to secure its oxidation

Phlogiston theory of combustion. The French chemist Lavoisier (1743–1794), who gave to oxygen its name, was the first to show that combustion is due to union with oxygen. Previous to his time combustion was supposed to be due to the presence of a substance or principle called *phlogiston.* One substance was thought to be more combustible than another because it contained more phlogiston. Coal, for example, was thought to be very rich in phlogiston. The ashes left after combustion would not burn because all the phlogiston had escaped. If the phlogiston could be restored in any way, the substance would then become combustible again. Although this view seems absurd to us in the light of our present knowledge, it formerly had general acceptance. The discovery of oxygen led Lavoisier to investigate the subject, and through his experiments he arrived at the true explanation of combustion. The discovery of oxygen, together with the part it plays in combustion, is justly regarded as one of the most important discoveries in the history of chemistry. It marked the dawn of a new period in the growth of the science.

The definiteness of chemical processes. Throughout this chapter attention has been repeatedly directed to the fact that chemical processes involve definite weights of matter. For example, the composition of a number of compounds has been expressed in exact percentages, since experiment has shown that these always have precisely the composition stated, irrespective of the source from which they are obtained or the method by which they are prepared. After extensive investigation of a very large number of compounds, chemists have concluded that this constancy of composition is a characteristic of every true compound, and a statement of this characteristic is commonly called the *law of definite composition.*

In like manner, the chemical changes which compounds undergo are always perfectly definite under stated conditions. Thus, when potassium chlorate is heated, for every 100 g. decomposed there result 39.16 g. of oxygen and 60.84 g. of potassium chloride. When iron burns in oxygen, 100 g. of iron combines with 38.20 g. of oxygen to form 138.20 g. of oxide of iron. If less than 38.20 g. of oxygen is present, then a corresponding amount of iron will remain unchanged. On the other hand, if more than 38.20 g. of oxygen is present, then all the iron will be changed into the oxide, and the excess of oxygen will remain unaltered. The actual experiments which justify these conclusions will come before us from time to time as we proceed.

EXERCISES

In all the problems in this text which involve volumes of gases, it is understood that, unless otherwise designated, the volumes referred to are those which the gas will occupy at a temperature of 0° and under a pressure of 1 atmosphere.

1. In Fig. 9 why does the water stay in the inverted cylinder? Why does the oxygen displace it? When a little oxygen has entered, why does not all the water run out?

2. Suggest a method for collecting a gas that is soluble in water.

3. Why is it that the discovery of oxygen is ordinarily attributed to Priestley, although others had obtained it before him?

4. Report brief accounts of the lives of Priestley, Scheele, and Lavoisier (consult encyclopedia).

5. Can combustion take place without the evolution of light?

6. Is the evolution of light always produced by combustion?

7. Suggest a reason why wood in the form of shavings burns more rapidly than the same wood in the form of a log.

8. Why do substances burn more rapidly in pure oxygen than in air?

9. Inquire at a garage whether oxygen is used in connection with the repair of motor cars and, if so, for what purpose.

10. Suggest a reason why some metals tarnish on exposure to air, while others remain bright.

11. Consult the dictionary for the derivation and significance of the word *phlogiston.*

12. Calculate the weight in grams of 50 l. of oxygen measured at 0° and under a pressure of 1 atmosphere.

13. Calculate the weight in grams of each of the following compounds necessary for the preparation of 50 l. of oxygen: (1) mercuric oxide; (2) water; (3) potassium chlorate.

14. Calculate the volume of oxygen that would be evolved on heating 10 g. of potassium chlorate; 10 g. of mercuric oxide.

15. Assuming the cost of potassium chlorate and mercuric oxide to be respectively $0.50 and $1.50 per kilogram, calculate the cost of materials necessary for the preparation of 50 l. of oxygen from each of the above compounds.

16. 100 g. of potassium chlorate and 25 g. of manganese dioxide were heated in the preparation of oxygen. Give the weight of each of the products left in the flask.

CHAPTER IV

HYDROGEN

Historical. The element hydrogen was first clearly recognized as a distinct substance by the English investigator Cavendish, who in 1766 obtained it in a pure state and showed it to be different from the other inflammable airs or gases which had long been known. Because it had been found to be a constituent of water, Lavoisier gave it the name *hydrogen*, which means "water former."

Occurrence. In the free state hydrogen is found in the atmosphere, but only in traces (about 1 volume in from 15,000 to 20,000 volumes of air). In the combined state it is widely distributed, being a constituent of water as well as of all living organisms and the products derived from them, such as starch and sugar. About 10 per cent of the human body is hydrogen. Combined with carbon, it forms the substances which constitute petroleum and natural gas. It is an interesting fact that while hydrogen in the free state occurs only in traces on the earth, it occurs in enormous quantities in the gaseous matter surrounding the sun and certain other stars.

Preparation from water. Hydrogen can be prepared from water by several methods, the most important of which are the following:

1. ***By the electric current.*** As has been indicated in Chapter II, water is easily separated into its constituents, hydrogen and oxygen, by passing an electric current through it under certain conditions.

2. *By the action of certain metals.* When brought into contact with certain metals under appropriate conditions, water gives up a part or the whole of the hydrogen, the place of the hydrogen being taken by the metal. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a bit of sodium is thrown on water, an action is seen to take place at once, sufficient heat being generated to melt the sodium, which runs about on the surface of the water. The change which takes place consists in the displacement of one half of the hydrogen of the water by the sodium, and may be represented as follows:

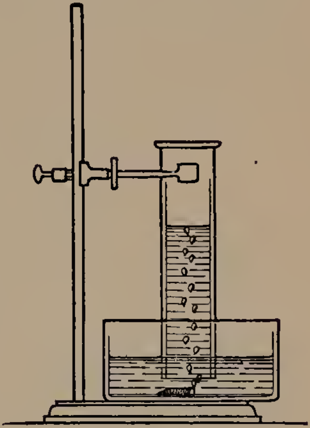


FIG. 14. The preparation of hydrogen by the action of sodium on water

$$\text{sodium} + \underset{\left[\begin{array}{l}\text{hydrogen}\\ \text{oxygen}\end{array}\right]}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\left[\begin{array}{l}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{array}\right]}{\text{sodium hydroxide}}$$

The sodium hydroxide formed is a white solid which remains dissolved in the excess of undecomposed water and may be obtained by evaporating the solution to dryness. The hydrogen is evolved as a gas and may be collected by suitable means.

A simple form of apparatus used in preparing hydrogen by the action of sodium on water is represented in Fig. 14. Since the sodium is lighter than water, it is kept under the water by pushing a pellet of the metal into the end of a short piece of lead tubing, the other end of which has been sealed. The tube containing the sodium is then dropped into a trough of water. Hydrogen is at once evolved and is collected by bringing over it a bottle or cylinder filled with water, as shown in the figure.

Other metals, such as magnesium and iron, decompose water rapidly but only at higher temperatures. When steam is passed over hot iron, for example, the iron combines with the oxygen of the steam, setting free all of the hydrogen. Experiments show that the change may be represented as follows:

$$\text{iron} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\begin{bmatrix}\text{iron}\\ \text{oxygen}\end{bmatrix}}{\text{iron oxide}}$$

The iron oxide formed is a reddish-black compound identical with that obtained by the combustion of iron in oxygen.

Preparation of hydrogen from iron and steam. The apparatus used in the preparation of hydrogen from iron and steam is shown in Fig. 15. A porcelain or iron tube *A*, about 50 cm. in length and 2 cm. or 3 cm. in diameter, is partly filled with fine iron wire or tacks and connected as shown in the figure. The tube is heated, slowly at first, until the iron is red-hot. Steam is then conducted through the tube by boiling the water in the flask *B*. The hot iron combines with the oxygen in the steam, setting free the hydrogen, which is collected over water in *C*.

Preparation from acids. A more convenient method for preparing hydrogen in the laboratory consists in liberating it from acids by the action of metals. For this purpose any of the metals which liberate hydrogen from water, but only these, may be employed. Usually zinc or iron is used. The acids commonly employed are either hydrochloric acid or sulfuric acid. The former is an aqueous solution of a gaseous compound (known as hydrogen chloride) which contains 2.76 per cent of hydrogen and 97.24 per cent of chlorine, while the latter is an aqueous solution of an oily liquid (known as hydrogen sulfate) which consists of 2.06 per cent of hydrogen, 32.69 per cent of sulfur, and 65.25 per cent of oxygen. To liberate hydrogen it is only necessary to bring the acid, properly diluted with water, into contact with the metal. The metal gradually passes into solution, while the hydrogen of the acid is in turn set free. The liberation of the hydrogen is indicated by the effervescence of the liquid. When zinc and sulfuric acid are used in the preparation, the reaction may be represented in a general way as follows:

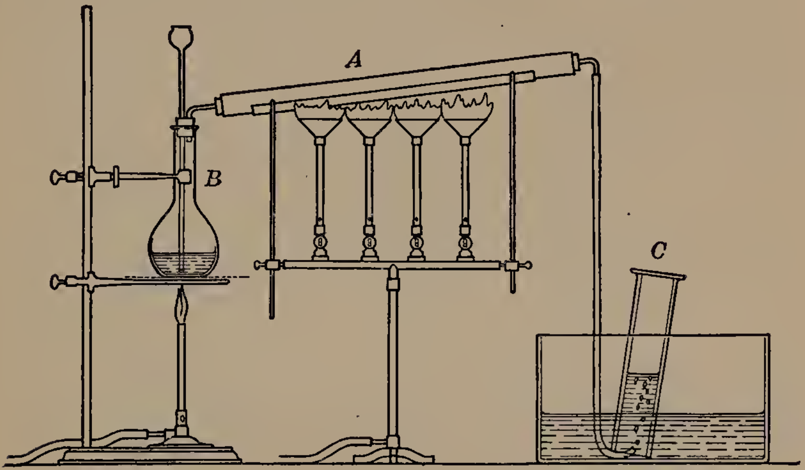


FIG. 15. The preparation of hydrogen by the action of iron on steam

$$\text{zinc} + \underset{\left[\begin{array}{l}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{array}\right]}{\text{sulfuric acid}} \longrightarrow \underset{\left[\begin{array}{l}\text{zinc}\\ \text{sulfur}\\ \text{oxygen}\end{array}\right]}{\text{zinc sulfate}} + \text{hydrogen}$$

It will be noted that the zinc simply takes the place of the hydrogen in the acid. The resulting compound of zinc, sulfur, and oxygen, known as zinc sulfate, is a white solid which remains dissolved in the water present.

When iron and hydrochloric acid are used in the preparation of hydrogen, the reaction may be represented as follows:

$$\text{iron} + \underset{\left[\begin{array}{l}\text{hydrogen}\\ \text{chlorine}\end{array}\right]}{\text{hydrochloric acid}} \longrightarrow \underset{\left[\begin{array}{l}\text{iron}\\ \text{chlorine}\end{array}\right]}{\text{iron chloride}} + \text{hydrogen}$$

Laboratory apparatus. A convenient form of apparatus for preparing hydrogen by the action of metals upon acids is shown in Fig. 16. The metal is placed in flask *A*, which is fitted with a stopper and connected with tubes, as shown in the figure. The acid, properly diluted with water, is added a little at a time through the funnel tube *B*. The liberated hydrogen escapes through *C* and is collected in receivers, as shown in the figure. The hydrogen which first escapes through the exit tube is mixed with the air originally present in flask *A*. *Such a mixture of hydrogen and air is violently explosive when brought in contact with a flame.* Therefore one must keep all flames away from the apparatus. Moreover, one should not collect the hydrogen until an amount of it has been generated sufficient to displace all the air previously contained in the flask.

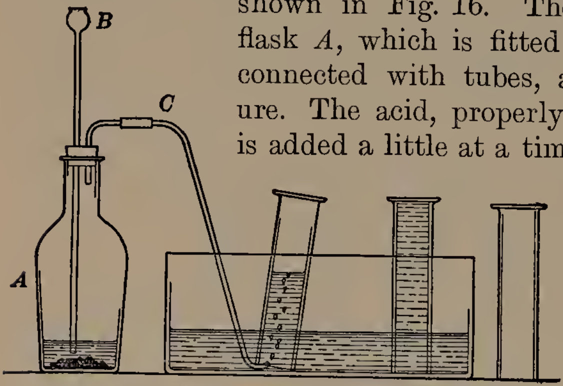


FIG. 16. The preparation of hydrogen by the action of metals on acids

A more convenient form of apparatus to use is that shown in Fig. 17. It is known as a Kipp generator and it has the advantage of being automatic in its action. The metal is placed in *A*, and the acid poured into *B*. When the stopcock *D* is opened, the acid runs down into *C* and up into *A*, where it comes in contact with the metal. The hydrogen generated escapes through *D*. If now the stopcock is closed, the hydrogen, being unable to escape through the tube, pushes the acid away from the metal in *A* down into *C* and up into *B*, so that the action ceases.

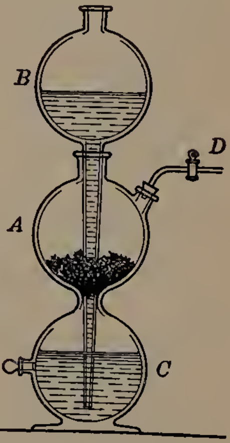


FIG. 17. A Kipp generator for preparing hydrogen

Commercial method for preparing hydrogen. A number of processes are being used for preparing hydrogen on a large scale, and new methods are being investigated in the hope of finding still cheaper ones. At present, in the United States, it is prepared from water, either by passing steam over hot iron (p. 40) or by decomposing the water by an electric current (p. 16). Another method, which is used in Europe, consists in distilling petroleum under definite conditions. Petroleum is composed largely of compounds of hydrogen and carbon, and when it is heated under proper conditions hydrogen is set free.

Properties of hydrogen. Hydrogen, like oxygen, is a colorless, odorless, and tasteless gas. One liter of it weighs 0.08987 g. It is the lightest of all known substances, being 14.385 times lighter than air; it may therefore be transferred from one vessel to another by pouring it upward, as shown in Fig. 18. The hydrogen in the cylinder *A* rises to the top of the cylinder *B* and forces the air out. The solubility of hydrogen in water is very small, being only about one half as great as that of oxygen.

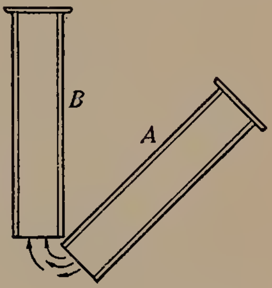


Fig. 18. Pouring hydrogen upward from one vessel into another

Dewar was the first to obtain hydrogen in the liquid state. He cooled the gas to a temperature of − 205° by means of liquid air, and at the same time subjected it to a pressure of 180 atmospheres. It was obtained as a colorless, transparent liquid, boiling at − 252.7°. This is the lightest liquid known, having a density of but 0.07 at its boiling point. When liquid hydrogen is evaporated under very small pressure, solid hydrogen is obtained as a snowlike body melting at about − 259°.

A number of the metals have the property of absorbing, or *occluding*, hydrogen. Most of the metals absorb only a small volume of the gas, but a few, such as gold, platinum, and palladium, absorb large volumes. One volume of finely powdered palladium absorbs over 800 volumes of the gas at ordinary temperatures.

Chemical conduct. At ordinary temperatures hydrogen is not an active element. Under suitable conditions, however, it combines with many of the elements, forming compounds known as *hydrides.* Thus, hydrogen and chlorine, when mixed together, will combine with explosive violence if heated or if exposed to the sunlight. The hydride formed in either case is called *hydrogen chloride.* Under suitable conditions hydrogen combines with nitrogen to form *ammonia*, and with sulfur to form the foul-smelling gas *hydrogen sulfide.* At ordinary temperatures hydrogen and oxygen may be mixed without apparent action. If the mixture is heated to about 800°, or if a flame is brought in contact with it, a violent explosion takes place. Nevertheless, under proper conditions hydrogen may be made to burn quietly in either oxygen or air. The resulting hydrogen flame is almost colorless and is very hot. The combustion of the hydrogen is due to its union with oxygen, and the product of the combustion is water. Experiments show that the ratio in which the two gases combine is 1 part of hydrogen to 7.94 of oxygen by weight. The heat liberated in the reaction amounts to 34,226 cal. for each gram of hydrogen entering into combination.

Directions for burning hydrogen. The combustion of hydrogen in air may be carried out safely as follows: The hydrogen is generated in the bottle *A* (Fig. 19), is dried by conducting it through the tube *B* filled with some substance (usually calcium chloride) which has a great attraction for moisture, and escapes through the tube *C*, the end of which is drawn out to a jet. *When all the air has been expelled from the apparatus the hydrogen may be ignited.* It then burns quietly, since only the small amount of it which escapes from the jet can come in contact with the oxygen of the air at any one time. By holding a cold dry bell jar or bottle *D* over the flame in the manner shown in the figure, the steam formed by the combustion of the hydrogen is condensed, and water collects in drops on the sides of the jar.

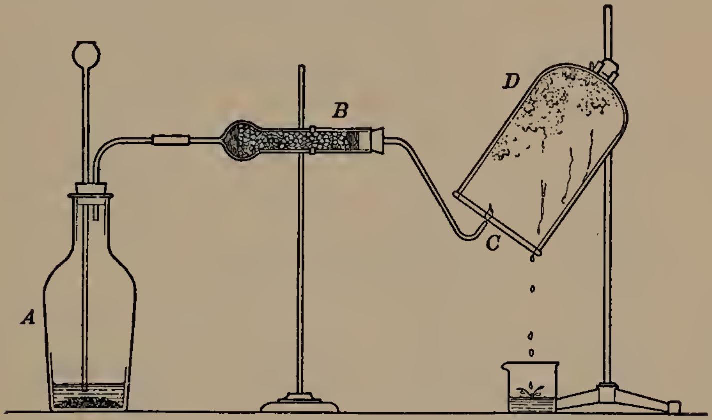


FIG. 19. Burning hydrogen and collecting the product of its combustion

Temperature at which hydrogen combines with oxygen. The union of hydrogen and oxygen probably takes place at ordinary temperatures, but the speed of the reaction is so slow that no combination can be detected even after long intervals of time. As the temperature is raised the speed increases. Thus, Meyer and Raum found that the two gases, when mixed in the proportion of two volumes of hydrogen to one volume of oxygen and heated to 100° for 218 days, showed no appreciable combination. When heated to 300° for 65 days it was found that, in different trials, from 0.4 per cent to 9.5 per cent of the mixture had combined. At 500° the change is still more rapid, but requires several hours for completion. At a temperature roughly approximating 800° the union of the two takes place with explosive violence. The temperature at which this instantaneous combination takes place is modified by very slight changes in the conditions, due to the catalytic effect of foreign substances, such as moisture and the materials of which the tube containing the gases is made. Certain catalyzers, such as finely divided platinum, bring about practically instantaneous combination at ordinary temperatures.

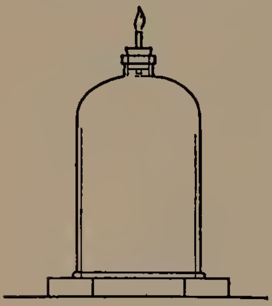


FIG. 20. Exploding a mixture of hydrogen and oxygen

A mixture of hydrogen and oxygen is explosive. That a mixture of hydrogen and air is explosive may be shown safely as follows: A cork through which passes a short glass tube about 1 cm. in diameter is fitted air-tight into the tubule of a bell jar (Fig. 20) of 2 l. or 3 l. capacity. (A thick glass bottle with the bottom removed may be used.) The tube is closed with a small rubber stopper and the bell jar filled with hydrogen, the gas being collected over water. When entirely filled with the gas the jar is removed from the water and supported by blocks of wood in order to leave the bottom open, as shown in Fig. 20. The stopper is now removed from the tube in the cork. The hydrogen, on account of its lightness, escapes from the tube and is at once lighted. As the hydrogen escapes, the air flows in at the bottom of the jar and mixes with the remaining portion of the hydrogen, so that a mixture of the two soon forms, and a loud explosion results. The explosion is not dangerous, since the bottom of the jar is open, thus leaving room for the expansion of the hot gas.


FIG. 21. Flame of a candle extinguished by hydrogen

Since air is only one fifth oxygen, the remainder being inert gases, it may readily be inferred that a mixture of hydrogen with pure oxygen would be far more explosive than a mixture of hydrogen with air. Such mixtures should not be made except in small quantities and by experienced workers.

Hydrogen does not support combustion. While hydrogen is readily combustible, it is not a good supporter of combustion; in other words, most substances will not burn in it. This may be shown by bringing a lighted candle supported by a stiff wire into a bottle or cylinder of the pure gas, as shown in Fig. 21. The hydrogen is ignited by the flame of the candle and burns at the mouth of the cylinder, where it comes in contact with the oxygen in the air. When the candle is thrust up into the gas, its flame is extinguished. If slowly withdrawn, the candle is relighted as it passes through the layer of burning hydrogen.

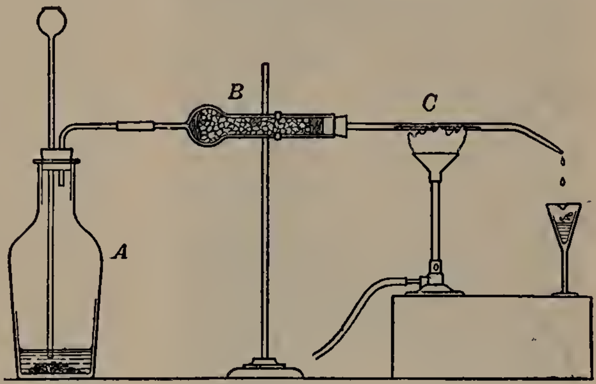


FIG. 22. The reduction of hot copper oxide by a stream of hydrogen

Reduction. On account of its tendency to combine with oxygen, hydrogen has the power of abstracting it from many of its compounds. Thus, if a stream of hydrogen generated in *A* (Fig. 22) and dried by passing through the tube *B* (filled with calcium chloride) is conducted through the tube *C*, which contains some copper oxide heated to a moderate temperature, the hydrogen abstracts the oxygen from the copper oxide. The change may be represented as follows:

$$\underset{\begin{bmatrix}\text{copper}\\ \text{oxygen}\end{bmatrix}}{\text{copper oxide}} + \text{hydrogen} \longrightarrow \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} + \text{copper}$$

The oxides of most of the metals act in a similar way. Thus, when hydrogen is passed over hot iron oxide, water and iron are formed:

$$\underset{\begin{bmatrix}\text{iron}\\ \text{oxygen}\end{bmatrix}}{\text{iron oxide}} + \text{hydrogen} \longrightarrow \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} + \text{iron}$$

In these reactions the oxide of the metal is said to undergo *reduction*. Reduction may be defined, therefore, as the process of removing oxygen from a compound. An element, such as hydrogen, which has a strong affinity for oxygen and which may be used for removing oxygen from a compound is termed a *reducing agent.*

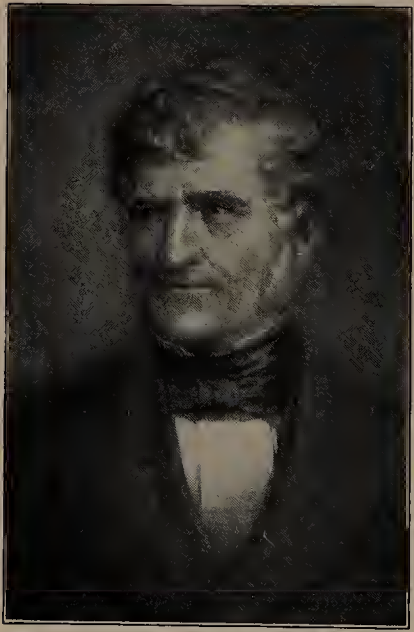


FIG. 23. Robert Hare (1781–1858)

An early American chemist; the inventor of many ingenious laboratory appliances, including the oxyhydrogen blowpipe

Relation of oxidation and reduction. It is evident from the statements concerning oxidation and reduction that the two processes are just the opposite of each other. The one process consists in the addition of oxygen to an element or compound, while the other consists in the removal of oxygen from a compound. Moreover it usually happens that when one substance is oxidized, some other substance is reduced. Thus, when hydrogen is passed over hot copper oxide (Fig. 22), the hydrogen is oxidized, while the copper oxide is reduced. It will be pointed out later that the terms *oxidation* and *reduction* are sometimes used with a broader meaning than those just given.

The oxyhydrogen blowpipe. This is a form of apparatus used for burning hydrogen in pure oxygen. It was devised and first used by an American scientist Robert Hare (Fig. 23) in the year 1801, in his laboratory in Philadelphia. As has been previously stated, the flame produced by the combustion of hydrogen in the air is very hot. It is evident that if pure oxygen is substituted for air, the temperature reached will be much higher, since there are no inert gases to absorb the heat. The oxyhydrogen blowpipe, used to effect this combination, consists of a small tube placed within a larger one, as shown in Fig. 24.

The hydrogen, stored under pressure, usually in steel cylinders, is first passed through the outer tube *H* (Fig. 24) and ignited at the open end of the tube *A*. The oxygen from a similar cylinder is then conducted through the inner tube *O*, and mixes with the hydrogen at the end of the tube. In order to produce the maximum heat, the hydrogen and oxygen must be admitted to the blowpipe in the exact proportion in which they combine; namely, 2 volumes of hydrogen to 1 of oxygen, or, by weight, 1 part of hydrogen to 7.94 parts of oxygen. The intensity of the heat may be shown by bringing into the flame pieces of metal such as iron wire or zinc. These burn with great brilliancy. Even platinum, which has a melting point of 1755°, may be melted by the heat of the flame.

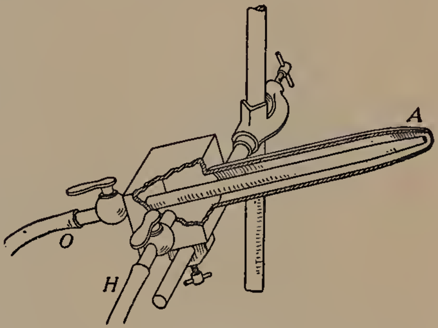


Fig. 24. The oxyhydrogen blowpipe

While the oxyhydrogen flame is intensely hot, it is almost nonluminous. If the flame is directed against some infusible substance like ordinary lime (calcium oxide), the heat is so intense that the lime becomes incandescent and glows with a brilliant light. This is sometimes used as a source of light, under the name of *Drummond light* or *limelight.*

The blast lamp. A similar form of apparatus is used in the laboratory as a source of heat under the name *blast lamp* (Fig. 25). This differs from the oxyhydrogen blowpipe only in the size of the tubes. In place of the hydrogen and oxygen the more accessible coal gas (or natural gas) and air are used. Coal gas and natural gas are composed largely of a mixture of gaseous compounds of carbon and hydrogen (Chap. XXV). While the temperature of the flame is not so high as that of the oxyhydrogen blowpipe, it nevertheless suffices for most chemical operations.

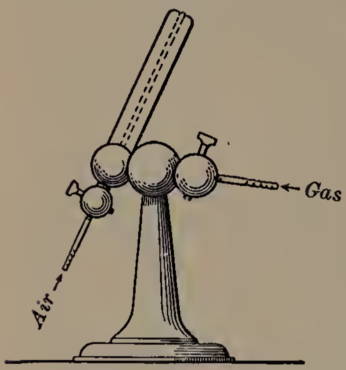


FIG. 25. The ordinary laboratory blast lamp

Exothermic and endothermic reactions. We have seen that in certain reactions a large amount of heat is given off. Examples of such reactions are the combustion of hydrogen in oxygen and the combustion of coal in air. All such reactions are said to be *exothermic.* In other reactions heat is continuously absorbed and so must be applied in order that the reaction may continue. Such reactions are termed *endothermic.* The decomposition of sugar is an example of an endothermic reaction.

Uses of hydrogen. Hydrogen is used as a material for the inflation of dirigible balloons such as are used in war. It has been used in the oxyhydrogen blowpipe as a source of light and heat, but this use has largely given way to more economical methods of producing high temperatures. (See the oxyacetylene blowpipe and the electric furnace.) It is also used as an agent for purifying certain oils, and for converting these oils into solid fats.

EXERCISES

1. Report the important events in the life of Cavendish (consult encyclopedia).

2. Will a definite weight of iron decompose an unlimited weight of steam?

3. Calculate the relative weight of hydrogen and oxygen (see weights of 1 l. of different gases, in Appendix).

4. Why is oxygen passed through the inner tube of the oxyhydrogen blowpipe rather than the outer?

5. What is the source of heat in the limelight?

6. In the experiment illustrated by Fig. 21, will the flame remain at the mouth of the cylinder?

7. Distinguish clearly between the following terms: *oxidation*, *reduction*, *combustion*, and *kindling temperature*.

8. Is oxidation always accompanied by reduction?

9. In the experiment illustrated by Fig. 19, why dry the hydrogen before burning it?

10. Suggest a way of determining the weight of the water formed in the reaction in the experiment illustrated by Fig. 22.

11. If hydrogen and oxygen unite in the ratio of 1 to 7.94 by weight, in what ratio do they unite by volume?

12. (*a*) How many calories of heat are evolved in the combustion of 100 l. of hydrogen to form water? (*b*) How many grams of water are formed?

13. How many grams of hydrogen can be obtained from 100 g. of hydrogen sulfate? What volume would this amount of hydrogen occupy?

14. A gas tank holds 250 l. of hydrogen. (*a*) What is the weight of this volume of hydrogen? (*b*) What weight of water would have to be decomposed by electricity in order to prepare this volume of hydrogen? (*c*) What volume of oxygen would be liberated in the process?

15. 10 g. of water is boiled and the steam passed over heated iron (Fig. 15). (*a*) What weight of hydrogen will be liberated? (*b*) What volume will the hydrogen occupy? (*c*) What change will take place in the weight of the iron?

CHAPTER V

THE GAS LAWS; THE KINETIC THEORY

Introduction. It will be remembered that in describing the properties of oxygen and hydrogen the weight of a liter of each gas was given. A moment's reflection will make it clear that these weights must be correct only under certain conditions, for it is a familiar fact that the volume of a given weight of a gas varies both with changes in pressure and with changes in temperature.

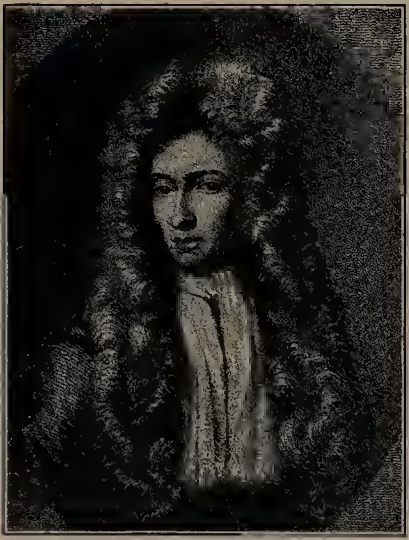


Fig. 26. Robert Boyle (1627–1691)

One of the most accurate of the early experimenters in chemistry and physics

Variation of volume with pressure: law of Boyle. That the volume occupied by a given weight of gas can be altered by changing the pressure is familiar to everyone who has pumped air into a bicycle or automobile tire. As early as 1660 Robert Boyle, an Irish investigator (Fig. 26), showed that the following statement correctly expresses the relation between volume and pressure. *If the temperature remains constant, the volume occupied by a given weight of a gas varies inversely as the pressure to which it is subjected.*

This generalization is known as *Boyle's law*. Thus, if a given weight of a gas occupies a volume of 1000 cc. when subjected to a certain pressure, it will occupy a volume of 500 cc. if the pressure is doubled, or of 250 cc. if the pressure is made four times as great, or of 2000 cc. if the pressure is diminished one half. This means that for a given weight of gas the product of the pressure by the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by P and V, and under a different set by P_1 and V_1, Boyle's law may be stated thus:

$$PV = P_1V_1$$

Standard pressure. For practical purposes we must choose some standard pressure to which all gas volumes may be referred. This is most conveniently chosen as the average pressure of the atmosphere at the sea level. This is equal to 1033.3 g. per square centimeter. In place of expressing the pressure in this way it is much more convenient to express it in terms of the height of the column of mercury which the pressure of the atmosphere will sustain. Expressed in this way the standard pressure is equal to that exerted by a column of mercury 760 mm. in height — this being the average height of the barometer at the sea level.

Illustration of the law of Boyle. A typical example will make the meaning of this law clear. Suppose that a gas, measured under a pressure of 720 mm., has a volume of 620 cc. What volume will this gas occupy under standard pressure (760 mm.), the temperature remaining constant?

According to Boyle's law, $PV = P_1V_1$. Substituting the values given in the problem, we have $760 \times V = 720 \times 620$; or $V = 587.4$ cc.

Variation of volume with temperature. If the pressure is held constant, all gases expand when the temperature is raised and contract when it is lowered, and it is a remarkable fact that the volumes of all gases change to the same extent for a given variation in the temperature. Let us suppose that the volume of a gas has been measured at zero on the centigrade scale. Experiment has shown that a rise of one degree causes an expansion of $\frac{1}{273}$ of this volume; a rise of five degrees, an expansion of $\frac{5}{273}$. If we take 273 cc. of this gas at zero, the volume at 1° above will be 274 cc.; at 1° below it will be 272 cc.; and at 5° below it will be 268 cc. At the same rate of contraction the volume will be 1 cc. at – 272°, and at – 273° it will be zero. Of course this cannot really happen, and experiment shows that before this temperature is reached, all gases have changed into liquids or solids. Helium, the most difficult gas to liquefy, passes into a liquid at – 268.7°.

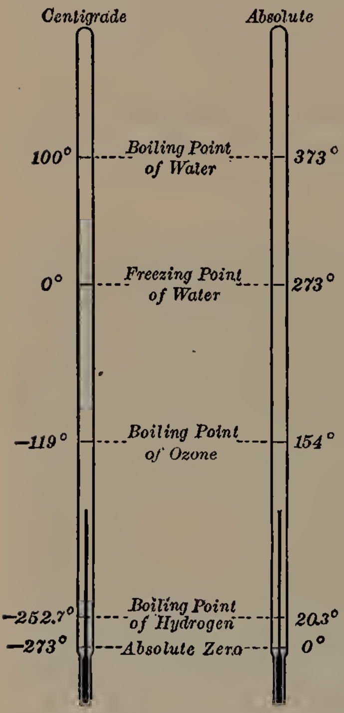


FIG. 27. Comparison of the centigrade with the absolute scale of temperature

The absolute scale of temperature. If we were to construct a thermometer having divisions of the same size as those on the centigrade scale, but with the zero point at – 273° on the latter scale, then the point at which water freezes (0° centigrade) would be 273°. At 272° on this scale the 273 cc. of gas mentioned in the last paragraph would measure 272 cc.; at 271° it would measure

271 cc.; at 1°, 1 cc. On such a scale the volume of a gas would be proportional to the temperature at every point. This scale is known as the *scale of absolute temperature*, the point − 273° centigrade being the *absolute-zero point*. Evidently the absolute temperature may be obtained by adding 273° to the centigrade reading. Thus 30° centigrade (C.) equals 30° + 273° (or 303°) absolute (A.). Fig. 27 gives a comparison of the centigrade and absolute scales at a number of temperatures.

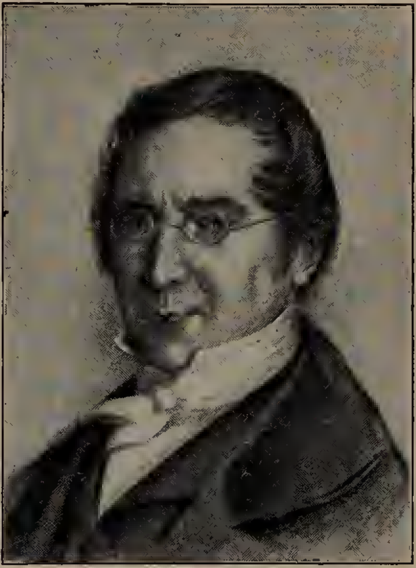


FIG. 28. Joseph Louis Gay-Lussac (1778–1850)

A distinguished French chemist who contributed much to our knowledge of gases and their combining ratios

The law of Gay-Lussac (or of Charles). A general statement can now be made in regard to the effect of temperature on the volume of a gas: *If the pressure remains constant, the volumes occupied by a given weight of a gas at different temperatures are directly proportional to the absolute temperatures of the gas.*

If V and V_1 are the volumes at the temperatures T and T_1 respectively, then we have the following proportion:

$$\frac{V}{V_1} = \frac{T}{T_1}$$

The above generalization is called the law of Gay-Lussac (Fig. 28) or of Charles, since it was formulated independently by these two Frenchmen in 1801.

Illustration of the law of Gay-Lussac. The following example will make the meaning of the law clear. The volume of a certain gas measured at a temperature of 70° is 650 cc. What will be its volume at 10°?

First reduce the centigrade readings to absolute:

$$70° \text{ C.} = 70 + 273 = 343° \text{ A.}; \quad 10° \text{ C.} = 10 + 273 = 283° \text{ A.}$$

Now substituting the appropriate values in the above equation, we have

$$\frac{V}{650} = \frac{283}{343}; \text{ or } V = 536.3 \text{ cc.}$$

Variations in volume due to changes both in pressure and temperature. In case both pressure and temperature change, then the correction may be made for each in succession, as illustrated in the following example:

A certain weight of gas measured 500 cc. at a temperature of 100° when subjected to a pressure of 760 mm. Calculate the volume which this gas will occupy at a temperature of 50° and a pressure of 740 mm.

First make the correction for pressure:

$$PV = P_1V_1$$

$$740 \times V = 760 \times 500; \text{ or } V = 513.5 \text{ cc.}$$

Next make the correction for temperature:

$$\frac{V}{V_1} = \frac{T}{T_1}; \text{ or } \frac{V}{513.5} = \frac{323}{373}; \text{ or } V = 444.6 \text{ cc.}$$

Standard conditions. Since the volume of a gas varies with both temperature and pressure, it is essential that we select both a standard temperature and a standard pressure to which all gas volumes may be referred. We have already noted that the standard pressure adopted is that exerted by a column of mercury 760 mm. in height. As a standard temperature, the temperature of melting ice is chosen. This is 0° centigrade or 273° absolute. Whenever the volume of a gas is given, unless otherwise specified, it is always assumed that the volume given is that occupied by the gas under standard conditions.

Standard conditions and laboratory conditions. The conditions of temperature and pressure which prevail in the laboratory are never the standard conditions. Knowing the volume of a gas under laboratory conditions, however, it is a simple matter to calculate the volume which the gas will occupy under standard conditions. The following problem will illustrate the method:

A gas measured 300 cc. under a pressure of 740 mm. and a temperature of 25° (or 298° A.). What will its volume be under standard conditions (0° and 760 mm. pressure)?

First find the change in volume due to change in pressure:

$$300 \times 740 = 760 \times V; \text{ or } V = 292 \text{ cc.}$$

Next make the correction for temperature:

$$\frac{V}{292} = \frac{273}{298}; \text{ or } V = 267.5 \text{ cc.}$$

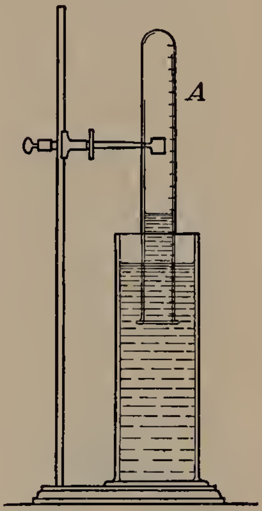


FIG. 29. Measuring the volume of a gas collected over a liquid

Aqueous vapor pressure. As a rule gases are measured in the laboratory by collecting them over water in a graduated tube as shown in Fig. 29. For example, if we wish to measure the volume of oxygen evolved in a certain reaction, the gas is conducted into the tube *A*, which has been previously filled with water and inverted in a cylinder of water as shown in the figure. In this process, however, a certain definite amount of water vapor (depending upon the temperature) passes into the tube along with the oxygen, so that the observed volume of the gas in the tube is the sum of the volumes of the oxygen and of the water vapor.

Correction for aqueous vapor pressure. The volume which the pure oxygen will occupy under any definite conditions of temperature and pressure may be determined as follows:

The tube *A* (Fig. 29) is first raised or lowered until the level of the water within and without the tube is the same. Under these conditions the pressure exerted by the atmosphere upon the surface of the water in the cylinder, and tending to force the liquid up into the tube *A*, is in equilibrium with the sum of the pressures exerted by the water vapor and the oxygen within the tube *A* and tending to prevent the water from rising in the tube. If we imagine the water vapor to be suddenly removed, but the volume to be kept unchanged, it is evident that the oxygen would occupy the entire volume, and that it would exert a pressure equal to the atmospheric pressure *less* the pressure that had been exerted by the water vapor within the tube. If we know the latter pressure, we can subtract it from the atmospheric pressure and so obtain the pressure exerted by the oxygen alone at the given temperature. The pressure of water vapor for all ordinary temperatures has been determined, and a table of such pressures is given in the Appendix. The pressures are expressed for convenience in terms of the height of a column of mercury which the pressure will sustain.

Example of correction for the pressure of water vapor. We are now in a position to make correction for the pressure of water vapor, and an example will make the procedure clear:

Let us suppose that a gas collected over water measures 300 cc. under a pressure of 740 mm. (as indicated by the barometric reading) and a temperature of 25° (298° absolute scale). Calculate the volume which the pure gas will occupy under standard conditions (0° and 760 mm. pressure).

First find the change in volume due to change in pressure. The gas collected over water is subjected to a pressure of 740 mm. less the pressure exerted by the aqueous vapor at 25°; namely, 23.69 mm.; $740 - 23.69 = 716.31$. Now apply the law of Boyle:

$$300 \times 716.31 = 760 \times V; \text{ or } V = 282.7 \text{ cc.}$$

Next make the correction for temperature:

$$\frac{V}{282.7} = \frac{273}{298}; \text{ or } V = 258.9 \text{ cc.}$$

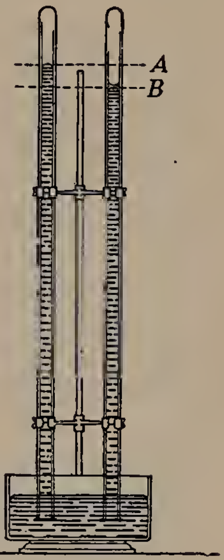


FIG. 30. Method of measuring the vapor pressure of a liquid

Determination of vapor pressure. The pressure of the vapor of a liquid at any temperature may be determined experimentally in the following way: Two long barometer tubes are filled with mercury and inverted in an open vessel of the same liquid (Fig. 30). A few drops of the liquid to be examined are introduced under the open end of one of the tubes, the liquid so introduced immediately rising to the top of the mercury column. Evaporation at once takes place and, because of the pressure of the gas so formed, the mercury column falls to some extent. When equilibrium is reached, the difference in level of the mercury in the two tubes, included between the dotted lines *A* and *B* in the figure, will correspond to the pressure of the vapor of the liquid expressed in millimeters of mercury. The tubes may be surrounded by jackets through which heated liquids are circulated, so that any desired temperature may be secured.

The meaning of laws in science. The law of Boyle and the law of Gay-Lussac are merely general statements in regard to the conduct of gases *as determined by experiment.* Like all other natural laws, they offer no explanation of the facts which they state, nor do they place any restriction upon nature which compels obedience, as the laws enacted by a legislature bind society. They are simply concise statements of what might be called the habits of nature as observed in experiment.

Forming a theory. It is certainly a very striking fact that all gaseous substances behave in so simple a manner, quite irrespective of their chemical nature. It would appear most probable that this must be due to some very simple mechanical structure which all gases have in common, and the mind at once begins to imagine a mechanical model which, if real, would act in the same manner. The process of constructing a mental picture of this kind is called *forming a theory.* The theory which has proved to be the most satisfactory in connection with the properties of gases is known as the *kinetic theory.* It should be noticed that laws are deduced from experiment and express the undoubted truth, while theories are products of the imagination and are always open to error.

The kinetic theory. This theory imagines the following general assumptions to be true:

1. All gases are made up not of continuous matter but of extremely minute particles relatively far apart. These particles are called *molecules.* Millikan has calculated that 1 cc. of a gas under standard conditions contains 27.09 billion billion molecules. This assumption satisfactorily accounts for the fact that gases may be compressed, since pressure would merely crowd the molecules into a smaller space.

2. The molecules are constantly moving in straight lines with enormous velocities, and are hitting against each other and the sides of the containing vessel and rebounding. For example, the molecules of hydrogen gas move at a velocity of about a mile per second. This assumption makes it clear why gases tend to expand indefinitely; also why gases exert a pressure against the sides of any vessel filled with the gas.

3. The effect of heat upon a gas is to increase the velocity of the molecules. If the velocity of the molecules is increased, the gas will tend to expand, and this satisfactorily accounts for the relation between the volume of a gas and the temperature as stated in the law of Gay-Lussac.

4. For certain reasons that will be brought out in a later chapter, it is also assumed that all the molecules of any given gaseous element (or compound) have the same weight, but that the molecules of different elements have different weights; also that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This last assumption was advanced by the Italian physicist Avogadro and is known as *Avogadro's hypothesis* (p. 281).

Value of a theory. The value of such a theory as the kinetic theory is at once apparent. It presents a mental picture which assists the memory in retaining a great variety of facts. It suggests many experiments which otherwise might never be undertaken, for our first impulse, after forming such a theory, is to test it experimentally in every possible way. It enables us to form a probable opinion in cases where experiment has not yet made a definite decision. It often leads to the detection of errors which have crept into the body of our knowledge as the result of faulty experiments. There is, however, a real peril in accepting a theory. The whole picture may be wrong, yet it may seem so plausible that we rest contented with it and fail to see its faults. Its very plausibility may prevent us from making experiments which would disclose the error in the theory and put us on the right track.

All such theories are best regarded as mere conveniences. Doubtless they express the true nature of things in many cases, but in others they do not. They are useful so long as we regard them as conveniences, and open to constant revision and modification or to rejection as our knowledge grows; but they are a real disadvantage when we come to regard them as the final and unchangeable truth.

EXERCISES

1. Why does a balloon tend to fall at night and rise at midday?

2. Why is the bottom of a balloon left open and not tightly closed?

3. How can you change the readings on the Fahrenheit scale into readings on the centigrade scale?

4. What evidence can you give tending to show that the amount of water vapor taken up by the atmosphere increases with the temperature?

5. Why does the carburetor on a motor car have to be adjusted with changes in the atmospheric conditions, in order to secure the greatest efficiency?

6. A gas measures 200 cc. when subjected to a pressure of 740 mm. What volume will it occupy if the pressure is increased to 760 mm., the temperature remaining constant?

7. A gas measured 150 cc. in a laboratory in which the temperature was 18°. What volume would the gas occupy if the temperature is reduced to 0°, the pressure remaining constant?

8. A certain volume of gas is measured when the temperature is 20° and the pressure 740 mm. (*a*) At what temperature would its

volume be doubled, the pressure remaining constant? (*b*) At what pressure would its volume be doubled, the temperature remaining constant?

9. A certain weight of hydrogen, subjected to atmospheric pressure, occupied a volume of 1250 cc. in a laboratory in which the readings of the thermometer and barometer were 18° and 746 mm. respectively. (*a*) What volume would this gas occupy under standard conditions? (*b*) Calculate the weight of this volume of hydrogen.

10. A gas subjected to atmospheric pressure occupied a volume of 1000 cc. in a laboratory at 20° and 740 mm. The next day the temperature of the laboratory fell to 12°, while the barometric pressure increased to 752 mm. What volume did the gas occupy under these conditions?

11. (*a*) 2500 cc. of oxygen measured over water at 20° and 740 mm. would occupy what volume under standard conditions? (*b*) Calculate the weight of this volume of the gas. (*c*) What weight of potassium chlorate would be required to prepare this amount of oxygen?

12. I wish to prepare 100 l. of hydrogen, measured over water in a laboratory where the temperature and pressure are respectively 16° and 750 mm. What weight of hydrogen sulfate would be required?

13. Oxygen was compressed in a 50-liter cylinder at 20° until the pressure was equal to 100 atmospheres. What volume would this occupy under a pressure of 1 atmosphere, the temperature remaining constant?

14. Suppose that the cylinder of oxygen referred to in problem 13 were heated to 500° during a fire. What pressure would the gas exert at this temperature?

CHAPTER VI

WATER; HYDROGEN PEROXIDE

Historical. Following the discovery of hydrogen, Cavendish made a careful study of the properties of the gas. In the course of his experiments he exploded a mixture of hydrogen and oxygen and observed that a small amount of a dewlike substance was formed. He was able to obtain a sufficient amount of the liquid to make a study of its properties, and showed that it was pure water. Cavendish did not perceive the full meaning of his discovery, however, and it remained for Lavoisier, a few years later, to repeat and properly interpret the experiments of Cavendish. He proved beyond doubt that the water which Cavendish had obtained resulted from the union of the hydrogen and oxygen, and that water must be regarded as a compound of these two elements.

Occurrence. The great abundance and wide distribution of water are facts familiar to all. Vast areas of the colder regions of the globe are covered with it in the form of ice, while in the liquid state it covers about five sevenths of the earth's surface, reaching in some places a depth of nearly six miles. Large quantities occur in the soil, and as a vapor it is an essential constituent of the atmosphere. It likewise constitutes more than half the weight of living organisms. For example, nearly 70 per cent of the human body is water. The water content of some of the more common foods is given in the table on page 344.

Composition of natural waters. Water as it occurs in nature always contains more or less matter derived from the rocks and soils with which it comes in contact. When such water is evaporated, this matter is left behind in solid form. Even rain water, which is the purest natural water, contains dust particles and gases dissolved from the atmosphere. The foreign matter in natural waters is of two kinds; namely, *mineral* and *organic*.

1. ***Mineral matter.*** The amount and nature of the mineral substances present in any given water vary with the nature of the rocks and soil with which the water has been in contact. The mineral substances ordinarily present in fresh waters are common salt and compounds of calcium, magnesium, and iron. Water containing any considerable amounts of mineral matter does not form a lather with soap, and is termed *hard water*; or if a large amount of mineral matter is present, it is called a *mineral water*. Water containing little or no mineral matter, such as rain water, is termed *soft water*. One liter of an average river water contains about 0.175 g. of mineral matter. The water of the ocean contains about 40 g. of mineral matter to the liter, more than three fourths of which is common salt. The water of Great Salt Lake contains from 150 to 200 g. of mineral matter in 1 l.

2. ***Organic matter.*** In addition to mineral matter natural waters contain more or less organic matter in solution or held in suspension. This consists not only of inanimate matter, derived from the decay of organic bodies on the earth's surface or present in sewage, but also of certain forms of living microörganisms which usually accompany such products. Waters taken from shallow wells or streams in thickly populated districts are likely to contain a considerable quantity of such matter.

Effect upon health of the foreign matter in water. Since natural waters constitute the ordinary supply for drinking and household purposes, the effect of the foreign matter in such waters when taken into the system is a question of great importance. Experience has shown that the mineral matter commonly found in water is not, as a rule, injurious to health. In fact, the presence of a certain amount of such matter is probably advantageous, supplying a portion of the mineral constituents necessary for the formation of the solid tissues of the body.

The organic matter present in water consists of inanimate products as well as of living microörganisms. The amount of the former commonly present in a water used for drinking purposes is so small that it is virtually without effect upon health. On the other hand, the presence, in water, of any considerable number of microörganisms renders it dangerous as a drinking water. It is true that many of these organisms are without injurious effect, but it is likewise true that others are the direct cause of disease. It is known that a transmissible disease such as typhoid fever is due to certain microörganisms which find entrance into the body. *It is easily possible for these organisms to find their way, through sewage, from a person afflicted with the disease into a poorly protected water supply, and so contaminate the water. It is largely in this way that typhoid fever is spread.* The general conclusion may therefore be drawn that, save in exceptional cases, any sickness traceable to the water supply is due to the presence in the water, not of mineral matter, or even of inanimate organic matter, but to certain living microörganisms.

The detection of impurities in water. The total amount of solid matter present in any given water is easily determined by evaporating a definite volume of the water to dryness and weighing the residue. This residue may then be subjected to further investigation and the nature of the mineral matter determined. An examination of this kind is called a *mineral analysis.* Such an analysis is of importance in determining whether or not a water is adapted for manufacturing purposes, such as for use in a steam boiler.

On the other hand, if one wishes to determine whether a water is wholesome for drinking, a so-called *sanitary analysis* is required. Such an analysis includes not only the determination of the organic matter present in the water but also of the decomposition products formed by the decay of such matter (chiefly ammonia, nitrites, and nitrates). From what has been said it might be inferred that a bacteriological examination alone would be sufficient. While it is true that such an examination is of the greatest importance, it is equally true that the determination of the inanimate organic matter present, together with the products of its decomposition, is of great value and supplements the knowledge gained from a bacteriological examination; for the disease-producing organisms find their way into a water supply through the sewage or drains, and are therefore accompanied by other organic matter, the presence of which in a water supply at once indicates pollution. Such a water should therefore not be used, for, although it may be temporarily free from disease-producing organisms, the conditions are such that their introduction may take place at any time.

It may be added that the physical properties of a drinking water rarely give any conclusive evidence as to its purity. A water may be unfit for drinking and yet be perfectly clear and odorless. Neither can any reliance be placed on the simple methods sometimes given for testing the purity of water. Only the trained chemist and bacteriologist can carry out such methods of analysis as are trustworthy.

Purification of water. Three general methods are used for the purification of water; namely, *distillation*, *boiling*, and *filtration*.

1. ***Distillation.*** The most effective way of purifying ordinary water is by the process of distillation. This consists in boiling the water and condensing the resulting steam. In the laboratory the process is usually conducted as follows:

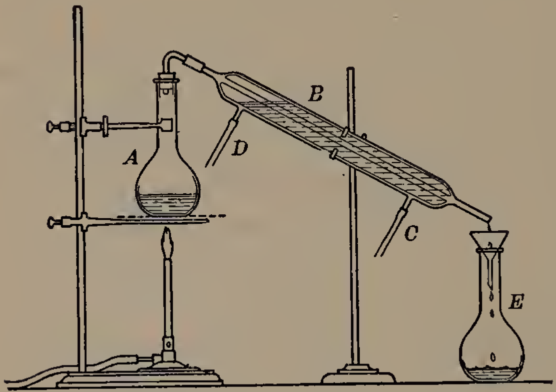


Fig. 31. The distillation of water as carried on in the laboratory

Ordinary water is poured into the flask *A* (Fig. 31) and boiled. The steam is conducted through the condenser *B*, commonly known as a Liebig condenser, which consists essentially of a narrow glass tube sealed within a larger one, the space between the two being filled with cold water, which enters at *C* and escapes at *D*. In this way the inner tube is kept cool and the steam in passing through it is condensed. The water formed by the condensation of the steam collects in the receiver *E*.

The water formed by the condensation of steam is known as *distilled water*. The mineral matter present in the original water is not volatile and remains in the container in which the water is boiled. The organic matter is also largely left in the container. A small amount of it, however, may be decomposed into volatile products, in which case these will pass over with the steam and be present in the distilled water. The percentage of such matter in distilled water is so small, however, that it is without effect in most of the chemical processes in which pure water is employed; in a very few cases where extreme purity is required, further treatment is necessary.

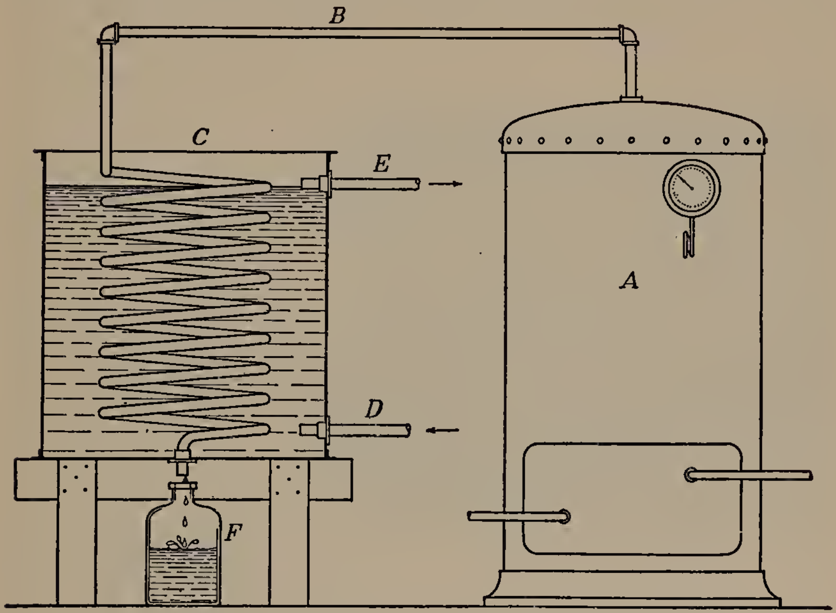


FIG. 32. The distillation of water for commercial purposes

Distilled water is used by the chemist in almost all of his work. Large quantities are also used in the manufacture of ice, as well as for drinking.

Commercial distillation. In preparing distilled water on a large scale the steam is generated in a metal boiler *A* (Fig. 32) and is conducted through the pipe *B* to the condensing coil *C*, made of tin. This pipe is wound into a spiral and is surrounded by cold water, which enters at *D* and flows out at *E*. The distilled water is collected in a suitable container *F*.

2. ***Boiling.*** In purifying water for drinking purposes it is only necessary to remove or destroy the microörganisms present. When the amount of water to be purified is small, as is the case with the household supply for drinking, this is most conveniently accomplished by boiling the water for ten or fifteen minutes. While the organisms are destroyed in a short time by moist heat, even severe cold has been found to have comparatively little effect upon them.

3. ***Filtration.*** On a small scale, water is filtered in two ways: (1) by passing it through some porous material, such as charcoal, or (2) by forcing it through porous clay ware, as is done in the Chamberlain-Pasteur filter. While such filters, if kept clean and in good condition, remove most of the organic matter, they do not remove mineral matter except such as is held in suspension. These household filters are not easily kept in order and soon become ineffective. They are no longer used to any great extent.

City filtration. Many cities find it necessary to take their water supply from rivers. The rivers in thickly populated districts are almost certain to be contaminated with organic matter, suggesting the possible presence of disease germs. Such water is a constant menace to the health of the city, so that it is of the greatest importance to find some way of purifying it effectively on a large scale. This is done by filtration. Two general kinds of filters are in use:

1. *Slow sand filters.* These consist of large beds of sand and gravel, through which the water passes slowly. Some of the impurities are strained out, while others are decomposed by the action of certain kinds of microörganisms which collect in a jellylike layer on the surface of the filter. The purified water passes into a porous pipe from which it is pumped into the city mains. The filters are covered to protect the water and prevent it from freezing.

2. *Mechanical filters.* In these the water, before filtration, is run into large tanks and mixed intimately with certain compounds, such as aluminium sulfate or iron sulfate, which form in the water a small amount of gelatinous solid. The water is then run into settling basins, where the gelatinous solid slowly settles to the bottom, carrying with it much of the organic matter present. The partially clarified water is then filtered through sand and gravel (Fig. 33). When this method is employed it is customary to add some germicide, such as chlorine (Fig. 77), to the water in order to destroy any microörganisms not removed by the gelatinous solid. The mechanical filter is largely replacing the slow sand filter, since the process is much more rapid and just as effective.

The effect of the filtration of the water supply upon the health of a city is shown by the fact that in general the number of cases of typhoid fever in cities which have introduced an effective water-purification system has been decreased by about 75 per cent.

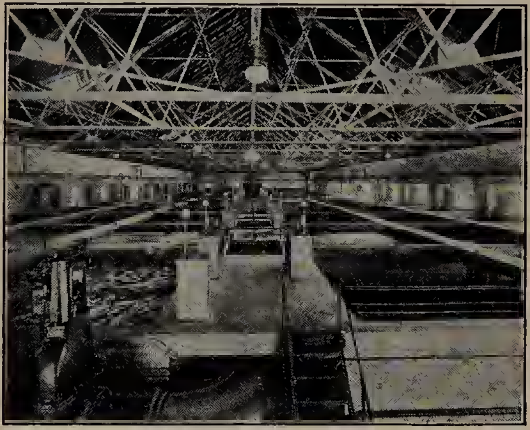


Fig. 33. Sand and gravel filter in a modern city filtration plant

Self-purification of water. It has long been known that water contaminated with organic matter tends to purify itself when exposed to the air (p. 34). This is due to the fact that air is somewhat soluble in water, and that the dissolved oxygen, in the presence of certain microörganisms, gradually oxidizes the organic matter present in the water; when this is destroyed, the organisms present die for lack of food. This process, however, cannot be relied upon to purify a contaminated water so as to render it safe for drinking purposes.

Properties of water. Pure water is an odorless and tasteless liquid, colorless in thin layers but having a bluish tinge when observed through a considerable thickness. It solidifies at 0° and boils at 100° under the normal pressure of 1 atmosphere. When water is cooled, it steadily contracts until the temperature of 4° is reached; at lower temperatures it expands. Water is remarkable for its ability to dissolve other substances, and is the most general solvent known. Even such substances as glass and various kinds of rocks which are ordinarily regarded as insoluble dissolve in water, but to a very limited extent. Chemists usually employ aqueous solutions of substances rather than the substances themselves, since, as a rule, chemical action takes place more readily in solution.

Chemical conduct. Water is a very stable substance; in other words, it does not undergo decomposition readily. To decompose it into its elements by heat alone requires a very high temperature. Even at 2500° only about 10 per cent of the water heated is decomposed. Though very stable toward heat, water can be decomposed in other ways, as by the action of the electric current or by certain metals.

Though containing 88.81 per cent of oxygen, water is not a good oxidizing agent, because of its great stability. However, certain metals, as well as carbon, can be oxidized by very hot steam, the hydrogen being set free. Water combines directly with many compounds, forming substances called *hydrates* (p. 251). Blue vitriol and alum are good examples of such hydrates.

Heat of formation and heat of decomposition are equal. The fact that a very high temperature is necessary to decompose water into hydrogen and oxygen is in accord with the fact that a great deal of heat is evolved by the union of hydrogen and oxygen (p. 49), for it has been proved that the heat necessary to decompose a compound into its elements (heat of decomposition) is equal to the heat evolved in the formation of the same compound from its elements (heat of formation).

The determination of the exact composition of water. Many very careful experiments have been made for the purpose of determining, with as great accuracy as possible, the ratio in which hydrogen and oxygen are present in water, and it is worth our while to study somewhat in detail the methods which have been employed, since they serve to illustrate in a general way the methods used in determining the composition of other compounds.

Two general methods of procedure are available for determining the composition of a compound: first, *the method of analysis*, in which a given weight of the compound is separated either directly or indirectly into its constituent elements and the identity and weight of each determined; second, *the method of synthesis*, which consists in determining the proportion in which the constituent elements unite to form the compound, and which is therefore just the opposite of analysis.

1. ***Methods based on analysis.*** It will be recalled that water may be easily decomposed into its constituents by the electric current. It would seem probable that the exact composition of water could easily be determined in this way, since the volumes of the gases liberated can readily be measured with accuracy, and if we know their densities, we can calculate their weights. When the experiment is carried out, however, the results obtained are not concordant, although in general the volume of the hydrogen liberated is slightly more than double the volume of the oxygen. Experiments prove that the method is subject to several sources of error. For example, the

water through which the liberated gases bubble dissolves more of the oxygen than of the hydrogen. The ratio between the amounts of hydrogen and oxygen obtained in this process, therefore, does not represent with great accuracy the ratio in which they are combined in water. More accurate results are obtained by the synthetic methods described in the succeeding paragraphs.

2. ***Methods based on synthesis.*** In the synthetic methods we determine the quantities of oxygen and hydrogen which combine directly to form water. A description of the method as carried out for purposes of illustration in the lecture room will serve to show the general principle involved.

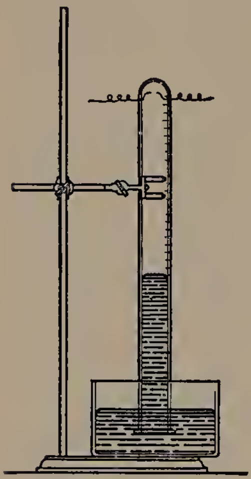


Fig. 34. A simple form of eudiometer

The combination of the two gases is brought about in a tube called a *eudiometer*. This is a graduated glass tube about 60 cm. long and 2 cm. wide, closed at one end (Fig. 34). Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a space of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one fourth filled. The tube is then lowered until the mercury stands at the same level inside and outside the tube, and the reading of the volume of the hydrogen is taken. Approximately an equal volume of pure oxygen is then introduced, and the volume is again taken. This gives the total volume of the two gases. From this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen.

The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube is at first depressed, because of the expansion of the gases due to the heat generated, but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations.

In order that the temperature of the residual gas and the mercury may become uniform, the apparatus is allowed to stand for a few minutes, and the volume of the gas is taken. The residual gas is then tested in order to ascertain whether it is hydrogen or oxygen, since experiments have proved that it is never a mixture of the two. From the information thus obtained the composition of the water may be calculated.

Calculation of composition. Thus, suppose the readings were as follows:

Volume of hydrogen	20.3 cc.
Volume of hydrogen and oxygen	38.7 cc.
Volume of oxygen	18.4 cc.
Volume of gas left after combination has taken place (found to be oxygen)	8.3 cc.

We have thus found that 20.3 cc. of hydrogen have combined with 18.4 cc. minus 8.3 cc. (or 10.1 cc.) of oxygen; or approximately 2 volumes of hydrogen have combined with 1 volume of oxygen. Since oxygen is 15.9 times as heavy as hydrogen, the proportion by weight in which the two gases combine is 1 part of hydrogen to 7.94 parts of oxygen.

A convenient form of eudiometer. A form of eudiometer represented in Fig. 35, and different from that shown in Fig. 34, is sometimes used, since it is easier by means of this to obtain the gases under the same conditions of temperature and pressure in order to make comparisons. With this apparatus it is easily possible to take the readings of the volumes under the same conditions of temperature and pressure, and thus compare them directly. The apparatus is filled with mercury and the gases introduced into the tube *A*. The experiment is carried out like the preceding one, except that, before taking the reading of the gas volumes, mercury is either added to the tube *B* or withdrawn from it by means of the stopcock *C*, until it stands at exactly the same height in both tubes. The gas inclosed in tube *A* is then under atmospheric pressure. The temperature of the gas, as well as the pressure to which it is subjected, being the same at the conclusion of the experiment as at the beginning, the volumes of the hydrogen and oxygen and of the residual gas may be directly compared as read off from the tube.

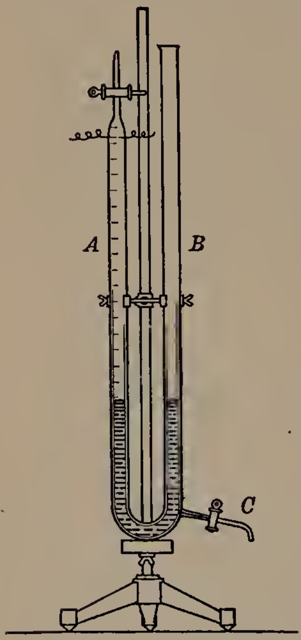


Fig. 35. A convenient form of eudiometer

Method used by Berzelius and Dumas. The work of Berzelius and Dumas is of interest from a historical standpoint, since they were the first to determine the composition of water with any great accuracy. The method used is a very ingenious one, the weights of the hydrogen and oxygen being determined by indirect methods and not by direct weighing of the gases, which is not easily done. The method was first used by Berzelius in 1820, and later, in 1843, with greater refinement, by Dumas.

Details of the experiment. Fig. 36 illustrates the essential parts of the apparatus used in making the determination. The glass tube *B* contains copper oxide, while the tubes *C* and *D* are filled with calcium chloride, a substance which has great affinity for water. The tubes *B* and *C*, including their contents, are carefully weighed, and the apparatus is connected as shown in the figure. A slow current of pure hydrogen is then passed through *A*, and that part of the tube *B* which contains copper oxide is carefully heated. The hydrogen combines with the oxygen of the copper oxide to form water, which is absorbed by the calcium chloride in tube *C*. The calcium chloride in tube *D* prevents any moisture entering tube *C* from the air. The operation is continued until an appreciable amount of water has been formed. The tubes *B* and *C* are then weighed once more. The loss of weight in the tube *B* will exactly equal the weight of oxygen taken up from the copper oxide in the formation of the water. The gain in weight in the tube *C* will exactly equal the weight of the water formed. The difference in these weights will of course equal the weight of the hydrogen present in the water formed during the experiment.

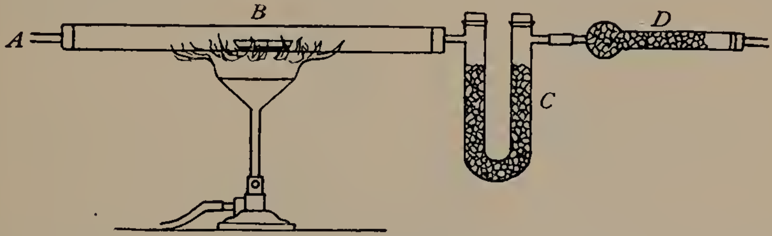


FIG. 36. Apparatus for determining the ratio by weight in which oxygen and hydrogen combine

Dumas's results The results secured by Dumas in 1843 may be summed up as follows:

Weight of water formed	945.439 g.
Oxygen given up by the copper oxide . . .	840.161 g.
Weight of hydrogen present in water . . .	105.278 g.

According to this experiment the ratio of hydrogen to oxygen in water is 105.278 : 840.161, or 1 : 7.98.

Morley's results. In recent years the American chemist Morley has determined the composition of water with great care. Extreme precautions were taken, and the hydrogen and oxygen which combined, as well as the water formed, were all accurately weighed. According to Morley's results, 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water.

Comparison of results obtained. From what has been described it is easy to see that it is by experiment alone that the composition of a compound can be determined. Different methods may lead to slightly different results. The more accurate the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is generally conceded by chemists that the results obtained by Morley in reference to the composition of water are the most accurate ones. In accordance with these results, then, water must be regarded as a compound containing hydrogen and oxygen in the ratio of 1 part by weight of hydrogen to 7.94 parts by weight of oxygen.

Relation between any given volume of water vapor and the volumes of the hydrogen and oxygen which combine to form it. When the quantitative synthesis of water is carried out at ordinary temperatures, the water vapor formed by the union of the hydrogen and oxygen at once condenses. The volume of the resulting liquid is so small that it may be disregarded in making the calculations. If, however, the experiment is carried out at a temperature of 100° or above, the water vapor formed is not condensed, and it then becomes possible to compare the volume of the vapor with the volumes of hydrogen and oxygen which combined to form it. In this way it has been proved that 2 volumes of hydrogen and 1 volume of oxygen combine to form exactly 2 volumes of water vapor, the volumes all being measured under the same conditions of temperature and pressure. It will be noted that the relation between these volumes may be expressed by whole numbers. It will be found from subsequent discussions that a similar statement holds in reference to all gaseous elements which combine with each other.

The form of apparatus used in determining the relation between the volumes of hydrogen and oxygen uniting and that of the aqueous vapor formed is illustrated in Fig. 37. The arm *A* of the eudiometer in which the combination of the gases is effected is surrounded by a tube through which is passed steam or, preferably, the vapor of some liquid boiling above 100° (amyl alcohol is often used). A mixture of 2 volumes of hydrogen with 1 of oxygen is introduced into the eudiometer. A suitable liquid is then boiled in the flask *B*. The resulting vapor is conducted through the space between the tube *A* and the outer tube and is then condensed as shown in the figure. When the volume of the mixed gases in *A* has become stationary, showing that the temperature of the gases is the same as that of the vapor, and the pressure adjusted as in the former experiment (see Fig. 35 and description), the reading on the eudiometer tube is noted. The union of the two gases is then effected by an electric spark from an induction coil *C*. After the union has taken place, the pressure is adjusted, and the reading again noted after the volume of the vapor has become constant. The volume of the vapor thus obtained can be compared directly with the volumes of the hydrogen and oxygen which united to form it.

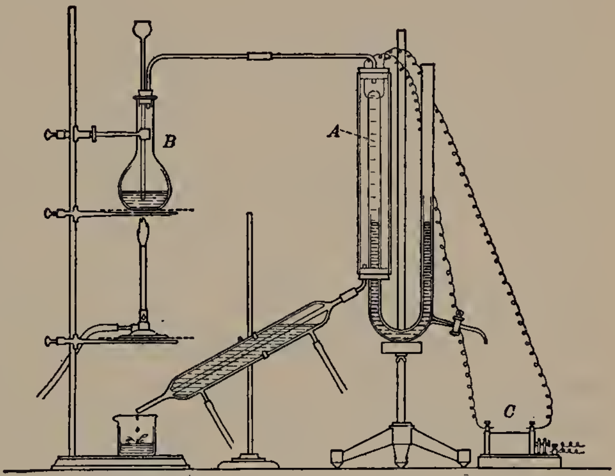


Fig. 37. Apparatus for determining the ratio by volume in which oxygen and hydrogen combine, and the ratio of each of these volumes to the volume of the steam formed

The law of definite composition. Attention has been called to the fact that chemical processes involve definite weights of matter (p. 35). We have now seen that chemically pure water has a perfectly definite composition. It makes no difference what the source of the water is. Whether it is obtained from the melting of pure ice, from the condensation of steam, or from the direct combination of hydrogen and oxygen, its composition is always exactly the same; namely, 1 part by weight of hydrogen and 7.94 parts by weight of oxygen, or, expressed in percentages, 11.19 per cent of hydrogen and 88.81 per cent of oxygen. A similar statement has been found to hold good for every pure compound. Thus, experiments have shown that potassium chlorate always contains 31.90 per cent of potassium, 28.94 per cent of chlorine, and 39.16 per cent of oxygen, while mercuric oxide contains 92.61 per cent of mercury and 7.39 per cent of oxygen. This truth regarding the constancy of composition of chemical compounds is known as the *law of definite composition*, and may be expressed as follows: *The composition of a pure compound is always precisely the same.*

History of law of definite composition. The common experiences of the earlier chemists led them to believe that the composition of a pure compound is quite definite. The question as to whether this is so or not became an important issue in the years 1802–1808, as a result of the views of a distinguished Frenchman, Berthollet. On theoretical grounds Berthollet was led to believe that the composition of a substance is somewhat variable, being dependent on the relative quantities of the several materials present at the time of its formation.

These views were strongly opposed by a fellow countryman, Proust, who was professor of chemistry at Madrid during most of the controversy. Proust maintained that the composition of a pure compound is perfectly definite, and that when two elements form more than one compound, each has its own exact composition, there being no intermediate gradations. He maintained that apparent variability is due to lack of purity in the compound. Proust's experimental work was very accurate for his time, but his analyses were subject to errors of from 1 to 2 per cent. The advance in experimental exactness has steadily demonstrated the correctness of Proust's conclusions. In 1860 and again in 1866 the Belgian chemist Stas undertook elaborate researches in a critical study of the law of definite composition, his analyses being trustworthy in some instances to within about 1 part in 50,000. Within these limits he showed that the law holds rigidly. In our own time the work of the American chemist Theodore Richards has demonstrated the accuracy of the law within still narrower limits.

Hydrogen peroxide. In 1818, while studying the action of acids upon certain oxides, the French chemist Thénard discovered the compound which we now call hydrogen peroxide. The pure compound is a liquid and, like water, is composed of hydrogen and oxygen. The proportions in which the hydrogen and oxygen are present in these two compounds, however, are widely different, as shown in the following statement:

Water	1 part of hydrogen to 7.94 parts of oxygen by weight
Hydrogen peroxide	1 part of hydrogen to 15.88 parts of oxygen by weight

In other words, the weight of oxygen *combined with a fixed weight of hydrogen* is just twice as great in hydrogen peroxide as in water. This larger percentage of oxygen is indicated by the name *peroxide*, the prefix *per* meaning "more" or "excess."

Preparation of hydrogen peroxide. While a dilute solution of hydrogen peroxide may be easily obtained, the pure compound cannot be prepared without great difficulty, since it decomposes into water and oxygen with explosive violence. Dilute solutions of the compound are prepared by the action of sulfuric acid on barium peroxide. The reaction may be represented as follows:

$$\underset{\begin{bmatrix}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{sulfuric acid}} + \underset{\begin{bmatrix}\text{barium}\\ \text{oxygen}\end{bmatrix}}{\text{barium peroxide}} \longrightarrow \underset{\begin{bmatrix}\text{barium}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{barium sulfate}} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{hydrogen peroxide}}$$

It will be noted that in this reaction the barium of the barium peroxide changes places with the hydrogen of the acid. The barium sulfate formed is insoluble, while the hydrogen peroxide dissolves in the water present. The barium sulfate may therefore be removed from the solution by filtration. In this way one can readily prepare a dilute solution of the peroxide in water. In this form it is a common article of commerce.

Properties of hydrogen peroxide. Hydrogen peroxide is a clear, sirupy liquid having a density of 1.458. Because of the highly explosive character of the pure compound it is prepared in the form of a dilute solution in water.

Since hydrogen peroxide so readily decomposes, with evolution of oxygen, it acts as a strong oxidizing agent, even in very dilute solutions. An easily oxidizable substance, like wool, is ignited by the addition of a few drops of the pure compound. The speed of decomposition of hydrogen peroxide is influenced in many ways. In dilute solutions and at a low temperature the speed is very slow, while at higher temperatures and in more concentrated solutions it becomes so great as to cause violent explosions. Moreover, the speed of decomposition is greatly affected by the presence of certain catalytic agents (p. 26). Thus a little finely divided platinum or manganese dioxide, added to a concentrated solution of the peroxide, produces such rapid decomposition as to cause an explosion. Certain organic substances have a similar action. Just as some substances increase the rapidity of decomposition, so others retard it. Thus the ordinary solution of hydrogen peroxide sold for medicinal purposes contains a small amount of some such substance, generally a trace of acid, which is added to preserve the strength of the solution by retarding decomposition.

Uses. Hydrogen peroxide has many commercial uses, all based on its strong oxidizing properties. The common medicinal peroxide of the druggist is an aqueous solution containing 3 per cent, by weight, of the compound. It has long been used as a germicide, but recent experiments indicate that its efficiency for this purpose has been greatly overrated. It acts upon certain dyes and natural colors, such as that of the hair, oxidizing them into colorless compounds; hence it is sometimes used as a bleaching agent. The chemist finds it especially useful as an oxidizing agent in many analytical operations. For this purpose it is often convenient to have a rather concentrated solution, so that a 30 per cent solution is now sold as a commercial product.

The law of multiple proportion. We have seen that both water and hydrogen peroxide are compounds of hydrogen and oxygen and that the ratio by weight in which these two elements are present in each of these compounds is as follows:

Water . . . . hydrogen : oxygen = 1 : 7.94
Hydrogen peroxide . . . . hydrogen : oxygen = 1 : 15.88

It will be seen that the ratio between the weights of oxygen combined with a fixed weight of hydrogen (say 1 g.) in these two compounds is 7.94 : 15.88, or 1 : 2.

Similarly, many elements other than oxygen and hydrogen unite to form a number of distinct compounds, each with its own precise composition. In all such compounds the same statement holds as in the case of water and hydrogen peroxide — the weights of the one element which are combined with a fixed weight of the other always bear a simple ratio to each other, such as 1 : 2 or 2 : 3. This truth is known as the *law of multiple proportion.* It was formulated by John Dalton (p. 89) in 1808, and may be stated thus: *When any two elements, A and B, combine to form more than one compound, the weights of A which unite with any fixed weight of B bear the ratio of small whole numbers to each other.*

EXERCISES

1. Why does the chemist use distilled water, rather than filtered water, in making solutions?

2. How could you determine the total amount of solid matter dissolved in a sample of water?

3. How could you determine whether a given sample of water is distilled water?

4. How could the presence of air dissolved in water be detected?

5. How could the amount of water in a food such as bread or potato be determined?

6. Would ice frozen from impure water necessarily be free from disease germs?

7. Suppose that the maximum density of water were at 0° instead of 4°; what effect would this have on the formation of ice on bodies of water?

8. In the experiment illustrated by Fig. 31, why is cold water passed into *C* instead of into *D*?

9. Mention at least two advantages that a metal condenser has over a glass condenser.

10. Draw a diagram of the apparatus used in your laboratory for supplying distilled water.

11. Report upon the method of purifying the water supply in your home town or city.

12. Determine the ratio in which oxygen and hydrogen unite from the following data, the volumes all being measured under the same conditions of temperature and pressure:

Volume of oxygen in eudiometer	8.54 cc.
Volume of oxygen and hydrogen	52.72 cc.
Volume of gas (hydrogen) left after explosion . .	27.10 cc.

13. Morley found the composition of water by determining the weights of hydrogen and of oxygen that combine with each other to form water. The results of six trials are as follows:

Hydrogen used	Oxygen used	Hydrogen used	Oxygen used
(1) 3.2645 g.	25.9176 g.	(4) 3.8450 g.	30.5294 g.
(2) 3.2559 g.	25.8531 g.	(5) 3.8382 g.	30.4700 g.
(3) 3.8193 g.	30.3210 g.	(6) 3.8523 g.	30.5818 g.

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

14. 20 cc. of hydrogen and 7 cc. of oxygen are placed in a eudiometer and the mixture exploded as in Fig. 37. (*a*) How many cubic centimeters of water vapor are formed? (*b*) What gas and how much of it remains in excess?

15. (*a*) What weight of water can be formed by the combustion of 100 l. of hydrogen, measured under standard conditions? (*b*) What volume of oxygen would be required in (*a*)? (*c*) What weight of potassium chlorate is necessary to prepare this amount of oxygen?

16. What weight of oxygen is present in 1 kg. of the ordinary hydrogen dioxide solution? In the decomposition of this weight of the dioxide into water and oxygen, what volume of oxygen (measured under standard conditions) is evolved?

CHAPTER VII

COMBINING WEIGHTS; THE ATOMIC THEORY

Introduction. We have already considered three laws which deal with the relations by weight which hold good during chemical action: (1) the law of conservation of matter, (2) the law of definite composition, (3) the law of multiple proportion. To these must now be added a fourth, — the *law of combining weights.*

Combining weights. We have seen that hydrogen and oxygen combine in two perfectly definite ratios by weight; namely, 1 g.: 7.94 g. and 1 g.: (2 × 7.94 g.). In a similar way it is easy to determine the ratios in which elements other than oxygen combine with hydrogen. For example, hydrogen combines with sulfur to form a gas called *hydrogen sulfide,* and with the metal calcium to form a solid called *calcium hydride.* In these compounds the ratios by weight are

Water	hydrogen 1 g., oxygen 7.94 g.
Hydrogen peroxide . .	hydrogen 1 g., oxygen 2 × 7.94 g.
Hydrogen sulfide . . .	hydrogen 1 g., sulfur 16 g.
Calcium hydride . . .	hydrogen 1 g., calcium 19.88 g.

It is therefore possible to assign to each element combining with hydrogen a number which expresses the weight in grams of the element which combines with 1 g. of hydrogen.

Now experiment reveals a very interesting fact. The numbers which express the ratios in which two elements combine with a fixed weight of *hydrogen* also express the ratio in which they combine with *each other.* Thus,

2 × 7.94 g. of oxygen combines with 16 g. of sulfur
7.94 g. of oxygen combines with 19.88 g. of calcium
19.88 g. of calcium combines with 16 g. of sulfur

From a study of a great number of combining ratios like those just given it has been determined that elements do not combine in simple ratios by weight, say 1 g. of one element with 1 g. or with 2 g. of another; but each element has a weight peculiar to itself that expresses how much of that element will combine with any other element. These numbers are called the *combining weights* of the elements.

Standard for combining weights. The numbers assigned to oxygen, calcium, and sulfur in the last paragraph were determined by finding how many grams of each of these elements combine with 1 g. of *hydrogen.* They are therefore relative to hydrogen taken as unity. Any other element might have been taken as the standard, and instead of 1 g. of the standard element any convenient weight might have been taken. The weights found are *ratio* weights, and while the weights will all be changed if we change the standard, their *ratios to each other* will remain the same. For many reasons it is better to select oxygen rather than hydrogen as the standard element. It is likewise better to select 8 g. rather than 1 g. as its standard value, so that no other element may have a combining weight of less than unity. If oxygen is taken as 8, hydrogen becomes 1.008; calcium, 20.03; and sulfur, 16.03.

The combining weight of an element may therefore be defined as that weight of the element which will combine with 8 g. of oxygen.

In Fig. 38 the lines connecting any two symbols at once indicate the ratio by weight in which the elements combine.

Elements with more than one combining weight. It is evident that some elements have more than one combining weight, for we have seen that 1 part of hydrogen combines either with 7.94 or with 15.88 parts of oxygen. Or, if we take 8 g. of oxygen as standard, the combining weight of hydrogen may be either 1.008 g. or 0.504 g. *In all such cases the number expressing the larger combining weight is a simple multiple of the number expressing the smaller combining weight.*

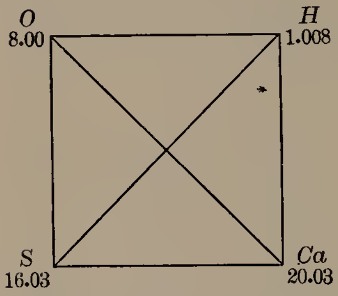


FIG. 38. Diagram showing the combining ratios of oxygen, hydrogen, sulfur, and calcium

The law of combining weights. The law of combining weights may now be stated as follows: *To each element may be assigned a number which in itself, or when multiplied by some integer, expresses the weight by which the element combines with other elements.*

The atomic theory. The four laws which in general terms state the way in which elements combine with each other are remarkably simple. We instinctively feel that the reason for this simplicity must lie in the way matter is made up, and we begin to imagine a structure for matter that if it were real would result in these simple laws. In other words, we try to devise a theory of the structure of matter and the mechanism of chemical action. Of all the theories that have been advanced concerning the nature of matter, the one proposed by John Dalton (Fig. 39), and known as the *atomic theory*, is the most satisfactory. The main points of this theory in its present form, together with the reasons for making them a part of the theory, are as follows:

1. Every weighable quantity of an elementary substance is made up of a very great number of unit bodies called *atoms.*

2. Experiment shows that the composition of a given compound is always the same (law of definite composition). The simplest way to adjust the theory of atoms to this fact is to assume that the atoms of each element all have the *same* weight, while those of different elements have *different* weights, and that during chemical union a definite number of one kind of atoms combines with a definite number of another kind to form a particle of a compound. If this should be true, a given compound would of necessity have a perfectly definite composition.

3. Since there is no change in weight when two substances act upon each other, the weights of the individual atoms must remain unchanged as a result of the action.

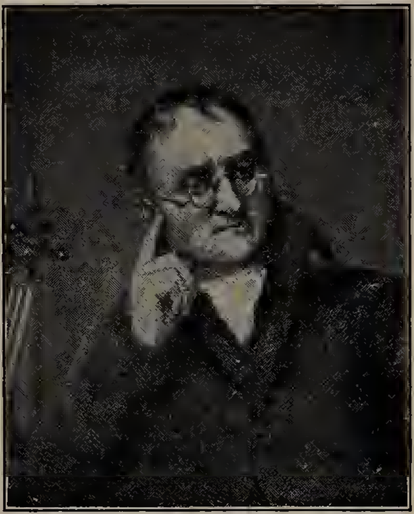


Fig. 39. John Dalton (1766–1844)

The English school-teacher and chemist who suggested the atomic theory

4. To account for the law of multiple proportion we must assume that the atoms of two different elements may unite in different ratios; for example, if one atom of *A* unites with one of *B* under one set of conditions, but with two of *B* under other conditions, then we shall have two different compounds. The masses of *B* combined with a fixed mass of *A* will be in the ratio of 1 : 2, since the number of atoms are in this ratio.

5. The law of combining weights tells us that a definite number can be assigned to each element, which expresses its combining value. If each atom has its own peculiar weight and if atoms always combine with each other in definite numbers, then these combining numbers indicate the *relative weights of the atoms themselves.* That an element may have two different combining weights, one a multiple of the other, is provided for by the supposition that the atoms are able to combine in several different ratios.

Summary of the atomic theory. The atomic theory suggests that all matter is made up of minute bodies called atoms. The atoms of a given element are all alike in weight, but those of different elements have different weights. When elements act upon each other, the action takes place between definite small numbers of the atoms.

While the atomic conception of matter is still referred to as the atomic theory, so many facts are now known that are in complete harmony with this view that it can hardly be doubted that this theory gives us a picture of real facts and that the reality of atoms and molecules is virtually a matter of conclusive proof.

Molecules and atoms. Dalton applied the name *atom* to both elements and compounds. It is evident, however, that the smallest particle of a compound must be made up of at least two different kinds of atoms. Thus the smallest particle of water that can be formed must contain both hydrogen and oxygen; such a particle of water is called a *molecule* of water, and any amount of water is simply a collection of a definite number of these molecules. In general, it may be said that the term *molecule* is now applied to the smallest particle which, taken in large numbers, makes up the bodies with which we deal.

Molecules of elements. Since two kinds of atoms unite to form a molecule of a compound, the question naturally arises, Do two or more atoms of the same kind combine to form a molecule of an elementary substance, or do elementary substances consist of separate atoms? It has been found that the elements differ among themselves in this respect. In some cases, as with mercury, the atoms do not unite, so that the molecule is the same as the atom; in other cases, as with oxygen and hydrogen, two atoms unite to form a molecule of the element. The experiments which prove that these statements are true will be described later.

Atomic weights. It would be of great interest if we could determine the actual weights of the various kinds of atoms. They are so very small, however, that we can never hope to determine their weight even approximately. It has been shown that the smallest particle visible with the most powerful microscope ever constructed contains at least 1000 atoms.

We have seen, however, that the ratio between the combining weights is the same as that between the weights of the atoms themselves, so we should be able to determine their *relative* weights with precision. But most of the elements have more than one combining weight, and we must find some means of choosing the one which correctly expresses the weight of a single atom.

Before this problem can be solved, methods must be devised for finding the relative weights of *molecules of compounds*. Such methods have been developed and will be described later (Chap. XXIII). These methods have led to the adoption of a single number for each element, called its *atomic weight*. A list of atomic weights will be found on the back cover of the book.

EXERCISES

1. Report the important events in the life of Dalton (consult encyclopedia).

2. State the four laws mentioned in this chapter.

3. Calculate the weights of hydrogen that combine with 100 g. of oxygen to form water and hydrogen peroxide respectively. Are your results in accord with the law of multiple proportion?

4. What is the derivation and meaning of the word *atom*? (Consult dictionary.)

5. Why did Dalton make the assumption that the atoms of the same element all have exactly the same weight?

6. What is meant by the following terms: (*a*) atom of an element; (*b*) molecule of an element; (*c*) molecule of a compound?

7. Would it be logical to speak of an atom of a compound?

CHAPTER VIII

FORMULAS; EQUATIONS; CALCULATIONS

Percentage composition. Just as we can determine the composition of water with great accuracy, so, by similar means, we can determine the composition of other compounds. Having analyzed a given compound, we usually express its composition in percentages, or in the parts of each element present in 100 parts of the compound. Thus, we have seen that water consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen.

Formulas. The plan of stating composition in percentages takes no account of the fact that compounds are made up of molecules in which each atom has a characteristic weight. It would be much better to have a method of stating composition which would express all these facts.

Since the molecule of any chemical compound consists of a definite number of atoms, it is very convenient to represent the composition of a compound by indicating the number and the variety of atoms that make up its molecules. This can be done by the use of symbols of the elements. In this way HgO will represent mercuric oxide, a molecule of which has been found to contain one atom of mercury (Hg) and one of oxygen (O). Similarly, H_2O will represent water, the molecules of which consist of two atoms of hydrogen and one of oxygen, the subscript figure indicating the number of atoms of the element whose symbol it follows. These combinations of symbols, which represent the atomic composition of molecules of substances, are called *formulas.*

Formulas from percentage composition. If we know the percentage composition of a compound as the result of analysis and can devise a method for determining the molecular weight of the compound, it will be easy to calculate its formula. Thus, if we know that potassium chlorate contains 31.90 per cent of potassium (K), 28.94 per cent of chlorine (Cl), and 39.16 per cent of oxygen (O), and that taking the weight of the oxygen atom as 16, the weight of a molecule of potassium chlorate is 122.56, we may reason as follows:

The portion of potassium in each molecule is 122.56 × 31.90 per cent = 39.10 K; the portion of chlorine is 122.56 × 28.94 per cent = 35.46 Cl; the portion of oxygen is 122.56 × 39.16 per cent = 48.00 O. Now the weight of the molecule (122.56) is the sum of the weights of the atoms that compose it. Therefore the numbers we have obtained are the weights of the several kinds of atoms composing the molecule, and these must be either the weights of the single atoms or of multiples of them. Reference to the table of atomic weights shows that the numbers obtained for potassium and for chlorine correspond to the weights for single atoms; while the weight found for oxygen is that of three atoms. Consequently the formula for potassium chlorate is $KClO_3$. Later we shall find general methods for obtaining molecular weights of compounds, and the formulas of the compounds can then be calculated by the above method.

Calculation of formulas when the molecular weight is not known. If we do not know the molecular weight of the compound, but merely have the percentage composition as found by analysis, we can determine the *simplest* formula the compound can have, but we cannot be sure that this is the *true* formula. As an example, let us suppose that we have found the percentage composition of potassium chlorate, but that we do not know that its molecular weight is 122.56.

The percentage numbers 31.90 per cent K, 28.94 per cent Cl, and 39.16 per cent O are the numbers of *grams* of these elements present in a purely arbitrary weight of potassium chlorate; namely, in 100 g. But we have seen that a gram of one element does not as a rule combine with a gram of another element, for they combine *in the ratio of their atomic weights.* Consequently the amount of each element present in 100 g. of a compound bears no simple relation to the atomic weights of the elements, and we wish to change the percentage numbers into others that will express the ratio between the *number* of the several kinds of *atoms* present in 100 g. If we divide the percentage number of each element by its atomic weight, the quotients will be the *relative number of each kind of atom* present in 100 g. of the compound.

31.90 ÷ 39.10 = 0.8158 = relative number of atoms of K in 100 g.
28.94 ÷ 35.46 = 0.8161 = relative number of atoms of Cl in 100 g.
39.16 ÷ 16 = 2.4475 = relative number of atoms of O in 100 g.

Now 100 g. of the compound is made up of a great number of molecules, and the *ratio* of the various atoms in a single molecule must be the same as in any weight of the compound. But in the molecule there cannot be fractions of atoms, but only the whole numbers. So we reduce the ratio 0.8158 : 0.8161 : 2.4475 to a ratio of whole numbers by dividing the three numbers by the least of the three. This gives us the ratio 1 : 1 : 3.

If this is the correct *ratio* of the number of the several kinds of atoms in the molecule, the *simplest* formula is $KClO_3$. Evidently the formula *might* be any multiple of this simplest formula such as $K_2Cl_2O_6$ or $K_3Cl_3O_9$, for compounds represented by any of these formulas would all give the same percentage composition. We should have to know the weight of the molecule to decide between these possibilities. Later we shall find ways to show that the molecular weight of potassium chlorate is somewhere near 120, so that the true formula is the simplest one; namely, $KClO_3$ (122.56).

Since the results of analysis are always subject to small errors, the percentage composition of a compound is never known from experiment with entire precision. Consequently the ratio for the number of atoms never comes out *exactly* an integer ratio, but it always comes so near to one as to leave no doubt as to the real ratio.

Facts expressed by formulas. From what has been said, it will be seen that formulas are used to express several distinct facts:

1. ***Atomic composition of molecules.*** A formula shows the number and kinds of atoms in a molecule of a compound. The formula H_2O states that a molecule of water is composed of two atoms of hydrogen and one of oxygen. The formula of hydrogen sulfate (H_2SO_4) shows that its molecule consists of two atoms of hydrogen, one of sulfur, and four of oxygen.

2. ***Molecular weights of compounds.*** Since each atom has its own weight, the sum of all the atoms in a molecule must be the weight of the molecule itself relative to oxygen taken as 16. The relative weight of the molecule of water is therefore $(2 \times 1.008) + 16 = 18.016$. The relative weight of the molecule of hydrogen sulfate (H_2SO_4) is $(2 \times 1.008) + 32.06 + (4 \times 16) = 98.076$.

3. ***Percentage composition of compounds.*** From a formula we can easily go back to the percentages from which it was calculated. Thus, if the molecule of water weighs 18.016 and contains one oxygen atom of weight 16, the fraction of its weight due to oxygen is $\frac{16}{18.016}$, or 88.81 per cent. The fraction due to hydrogen is $\frac{2.016}{18.016} = 11.19$ per cent.

Gram-molecular weights; formula weights. For practical purposes we deal with pounds or with grams of a substance, not with atoms and molecules. Now, since the numbers 18.016, 16, and 2.016 represent *the ratio by weight* between a molecule of water and the oxygen and hydrogen of which it is composed, the same ratios must hold between any weight of water we may choose and the oxygen and hydrogen in this weight of water, for any amount of water is simply a collection of molecules of water. Evidently, in 18.016 lb. of water there will be 16 lb. of oxygen and 2.016 lb. of hydrogen, and in 18.016 g. there will be 16 g. of oxygen and 2.016 g. of hydrogen.

For practical purposes, therefore, we may allow the symbol H to stand for 1.008 *grams* of hydrogen, the symbol O for 16 *grams* of oxygen, and the formula H_2O for 18.016 *grams* of water. The weight in grams of an element, corresponding to its atomic weight, is called a *gram-atomic weight* or *symbol weight.* The weight in grams of a compound, corresponding to its molecular weight, is called a *gram-molecular weight* or *formula weight.*

Equations. Having devised a convenient way of expressing the composition of compounds, not in percentages but in formulas, we make use of *equations* to express chemical transformations, using an arrow in place of an equality sign. For example, the equation

$$2H + O \longrightarrow H_2O \tag{1}$$

is a concise method of stating two distinct facts.

1. *Qualitatively*, it states that water is formed by the union of hydrogen and oxygen.

2. *Quantitatively*, it tells us that 2 symbol weights of hydrogen (2.016 g.) combine with 1 symbol weight of oxygen (16 g.) to form a formula weight of water (18.016 g.).

Molecular equations. Since a formula expresses the composition of a molecule, and since experiment has shown that a molecule of oxygen and one of hydrogen each contain two atoms, the formulas of these gases are written O_2 and H_2 rather than $2\,O$ or $2\,H$, which would simply represent two atoms not combined. If we wish equation (1) to state these additional facts, we shall have to change it to the form

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \qquad (2)$$

This is called a *molecular equation*, and it will be seen that it expresses the same ratios by weight as does equation (1). It also expresses the fact that 2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water, and this makes it a more useful equation.

Decomposition of potassium chlorate. Let us take another example. It will be remembered that oxygen was prepared by heating potassium chlorate, which has the formula $KClO_3$. When heated, this compound decomposes into oxygen and a compound called potassium chloride, whose formula is KCl. The decomposition is represented by the equation

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

This equation states the following facts:

1. *Qualitatively*, potassium chlorate decomposes into potassium choride and oxygen.

2. *Quantitatively*, 2 formula weights of potassium chlorate (2×122.6 g.) decompose into 2 formula weights of potassium chloride (2×74.69 g.) and 3 formula weights of oxygen (3×32 g.). The coefficient before a formula applies to the formula as a whole, while the subscript number applies only to the symbol which it follows.

3. *Molecularly*, 2 molecules of potassium chlorate decompose into 2 molecules of potassium chloride and 3 of oxygen.

Equations of reactions so far studied. Let us now put into the form of equations a number of the reactions studied up to this point, remembering that all of these equations rest upon careful experimental analysis.

1. *Preparation of oxygen:*

From mercuric oxide:

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

From potassium chlorate:

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

From the electrolysis of water:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

From sodium peroxide and water:

$$2\,Na_2O_2 + 2\,H_2O \longrightarrow 4\,NaOH + O_2$$

2. *Preparation of hydrogen:*

From sodium and water:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

From zinc and sulfuric acid:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

From iron and sulfuric acid:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

From steam and iron:

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2$$

3. *Preparation of hydrogen peroxide:*

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

Representation of the heat of reaction. We can also employ chemical equations to express the heat given off or absorbed during chemical action. The equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + 138{,}000 \text{ cal.}$$

states the fact that when 4.032 g. of hydrogen combines with 32 g. of oxygen, forming 36.032 g. of water, heat is given off to the extent of 138,000 cal. Evidently, when 1 formula weight (18.016 g.) of water is formed, 69,000 cal. is given off, and this is called the *heat of formation* of water.

Conditions of a reaction not indicated by equations. Equations merely state the composition of the substances taking part in the reaction and the weights of each one involved, together with the energy change measured as heat. They do not tell the conditions under which the reaction will take place. For example, the equation

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

does not tell us that it is necessary to keep heating the mercuric oxide to a moderately high temperature in order to effect its decomposition. The equation

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

in no way indicates that the hydrogen sulfate must be dissolved in water before it will act upon zinc. The equation

$$S + O_2 \longrightarrow SO_2$$

does not indicate that no perceptible action takes place unless the sulfur is first heated, but that when once started it goes on of its own accord and with a bright flame.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

Problems based on equations. Since an equation is a statement of the weights of materials which take part in a reaction, when the equation has once been established by experiment we can use it in calculating the various weights. A few examples will show how this may be done.

1. How many grams of oxygen will be evolved on heating 100 g. of mercuric oxide?

First write the equation for the reaction involved:

$$2\,HgO \longrightarrow 2\,Hg + O_2 \tag{1}$$

Next determine the relative weights of the amounts of the different substances involved in the reaction. The atomic weights of mercury and oxygen are respectively 200.6 and 16 (see table on back cover). Hence the relative weight of the $2\,HgO$ equals $2(200.6 + 16)$, or 433.2. Similarly, the relative weight of the oxygen evolved, namely, O_2, equals 2×16, or 32. It is convenient now to write these numbers under the formulas in equation (1). This then becomes

$$\underset{433.2}{2\,HgO} \longrightarrow 2\,Hg + \underset{32}{O_2}$$

These numbers indicate that 433.2 units by weight (in this case grams) of mercuric oxide will, on being heated, evolve 32 units by weight of oxygen; hence 1 g. of mercuric oxide will give $\frac{32}{433.2}$ g. of oxygen, and 100 g. will give $100 \times \frac{32}{433.2}$, or 7.38 g.; or the relation between the weights of the substances involved may be stated in the form of a proportion:

$$\frac{433.2}{32} = \frac{100}{x}$$

$$x = 7.38$$

2. I wish to prepare 100 g. of oxygen, using potassium chlorate as a source of the oxygen. How many grams of the chlorate will be required?

$$\underset{245.12}{2\,KClO_3} \longrightarrow 2\,KCl + \underset{96}{3\,O_2}$$

Proportion: $\frac{245.12}{96} = \frac{x}{100}$; or $x = 255.33$ g.

3. How many grams of zinc must be dissolved in sulfuric acid to produce 10 g. of hydrogen?

$$\underset{65.37}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{2.016}{H_2}$$

Proportion: $\frac{65.37}{2.016} = \frac{x}{10}$; or $x = 324.2$ g.

It must be remembered that the equations show relations by *weight*, not by volume; hence in problems involving volumes of gases it will be necessary first to find the weights of the gases. The table in the Appendix gives the weight of 1 l. of each of the common gases, measured under standard conditions. The following problem will illustrate the method:

4. How many grams of potassium chlorate are necessary to prepare 100 l. of oxygen?

Since 1 l. of oxygen weighs 1.429 g., 100 l. will weigh 142.9 g.

$$\underset{245.12}{2\,KClO_3} \longrightarrow 2\,KCl + \underset{96}{3\,O_2}$$

Proportion: $\frac{245.12}{96} = \frac{x}{142.9}$; or $x = 363.8$ g.

EXERCISES

1. State all the facts expressed by the formulas HCl, HNO_3, $Ca(OH)_2$, and H_3PO_4.

2. Calculate the percentage composition of the following compounds from the formulas as given: (*a*) potassium chlorate ($KClO_3$); (*b*) hydrogen sulfate (H_2SO_4); (*c*) water (H_2O); (*d*) saltpeter (KNO_3); (*e*) baking soda ($NaHCO_3$).

3. From the following analyses calculate the simplest formula:

(1)	S = 39.07%	O = 58.49%	H = 2.44%
(2)	Ca = 29.40%	S = 23.56%	O = 47.04%
(3)	K = 38.67%	N = 13.88%	O = 47.45%

4. It is required to prepare 30 g. of oxygen by heating mercuric oxide. How much oxide must be heated?

5. What weight of hydrogen will be obtained from the action of sulfuric acid on 100 g. of zinc? What will be its volume under standard conditions?

6. A given volume of oxygen standing over water at 20° and 745 mm. measures 10 l. (*a*) What would be its volume under

standard conditions? (*b*) What is its weight? (*c*) What weight of potassium chlorate would be required to prepare this amount of oxygen?

7. 100 cc. of sulfuric acid containing 20 g. of hydrogen sulfate (H_2SO_4) was added to 10 g. of zinc. Calculate the weight of hydrogen evolved.

8. When hydrogen is liberated by the action of zinc on sulfuric acid, what weight of zinc sulfate is formed for each gram of hydrogen liberated?

9. If you had 10 g. of iron with which to prepare hydrogen, would you heat it with steam or act upon it with sulfuric acid in order to obtain the maximum quantity of hydrogen?

10. What weight of potassium chlorate is necessary to furnish sufficient oxygen to fill four 200-cubic-centimeter bottles in your laboratory (the gas to be collected over water)?

11. Calculate the weight of the compounds necessary for preparing 10 kg. of the common medicinal hydrogen peroxide.

12. A bottle containing 1 kg. of medicinal hydrogen peroxide was set aside until the peroxide was completely decomposed into water and oxygen. (*a*) Calculate the volume of the oxygen evolved. (*b*) Calculate the weight of the water left in the bottle.

13. 10 g. of zinc was used in the preparation of hydrogen. What weight of iron will be required to prepare an equal volume of the gas?

14. 1 kg. of potassium chlorate was heated until all the oxygen was evolved. Calculate the weight of the potassium chloride left.

15. A certain Zeppelin airship was found to have a capacity of 25,000 cu. yd. Supposing that the hydrogen used in inflating this is made by the action of sulfuric acid on iron, calculate the weight of hydrogen sulfate and iron necessary to inflate this airship at 20° and 740 mm. (1 yd. = 0.9144 m.).

CHAPTER IX

THE THREE STATES OF MATTER

Gases, liquids, and solids. We have found that water exists in three very different states; namely, as gas, as liquid, and as solid. In a general way these three states may be described by saying that a gas (or vapor) is that form of matter that tends to distribute itself uniformly throughout the space in which it is placed. A liquid collects in the bottom of the containing vessel; it has no characteristic form of its own, but takes the shape of the vessel in which it is placed. A solid retains its own form irrespective of the shape of the vessel. Most substances can be obtained in all these states.

Evaporation. When a liquid such as water is placed in an open vessel, it gradually passes into the air in gaseous form, or *evaporates*. In a confined space, as in a partly filled bottle, evaporation takes place until the air above the liquid contains a definite percentage of vapor, or becomes *saturated* with the vapor. The process of evaporation does not really cease when saturation is reached, but the rate at which the vapor is formed from the liquid is just balanced by the rate at which the vapor condenses to form the liquid. Saturation is therefore a balance between these two rates.

If the liquid is now warmed, the rate of evaporation is increased. A new balance is reached at this higher temperature with a higher percentage of vapor present in the air than there was before. The vapor formed from the liquid is a gas and, like any other gas, exerts a pressure upon the walls of the containing vessel and upon the surface of the liquid. This is spoken of as the *vapor pressure of the liquid*, although it would be more exact to call it the *pressure of the vapor of the liquid.* Solids as well as liquids evaporate, as is shown by the odor of such substances as camphor and naphthalene (moth balls).

Relative humidity. The phrase *relative humidity* is familiar in the government weather reports. By the humidity at a given time is meant the percentage of water vapor in the air as compared with the percentage present at saturation at the same temperature. To be comfortable, air should be about 70 per cent saturated.

Boiling point. While a liquid is being heated, a part of the heat energy added to it is used in raising its temperature by increasing the motion of the molecules of the liquid; a part is absorbed in converting the liquid into vapor against the attraction of the molecules that tends to hold it together as a liquid. The formation of this vapor is opposed by the pressure of the atmosphere. When the pressure of the vapor just above the liquid becomes great enough to overcome the pressure of the atmosphere, the air is pushed back by the vapor. All the heat energy supplied to the liquid is now used in changing the liquid into vapor and in the mechanical work of pushing back the atmosphere, and the temperature ceases to rise. If the opposing atmospheric pressure is increased, the liquid must be heated to a higher temperature before its vapor pressure will exceed the higher pressure. The temperature at which the pressure of the vapor just exceeds the pressure of the atmosphere is called the *boiling point* of the liquid. It will be seen that the point changes with the pressure. Under a pressure of 760 mm. water boils at 100°; under a pressure of 525.5 mm. it boils at 90°.

Heat of vaporization and of condensation. The quantity of heat required to change 1 g. of a liquid *at its boiling point* into 1 g. of vapor at the same temperature is called the *heat of vaporization*. For water this is unusually large, and amounts to 539 cal. If a gas is maintained at a pressure of 760 mm. and is gradually cooled, condensation into a liquid will begin when the boiling point is reached. During condensation the temperature remains constant and the quantity of heat given out in the process (*heat of condensation*) is exactly equal to the heat of vaporization. Since the heat given out tends to oppose the process taking place, condensation is not rapid unless some method is devised for absorbing the heat. This is usually accomplished by passing the vapor through a condenser.

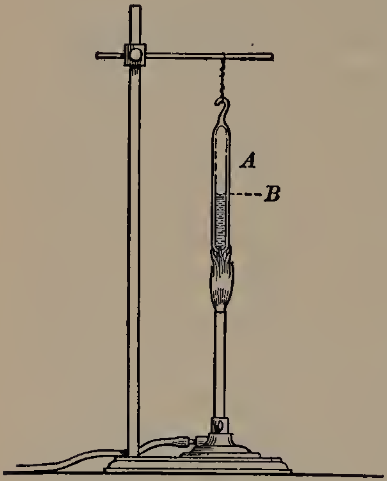


Fig. 40. The critical temperature of a liquid

Critical point. If a liquid is sealed within a tube from which all air has been withdrawn, *A* (Fig. 40), the lower end of the tube will be filled with liquid and the upper end with vapor. If the liquid is now heated by a burner, it cannot boil, for the pressure of its vapor cannot overcome the opposing pressure and escape. As the heating progresses, more and more of the liquid is vaporized. The density of the remaining liquid diminishes, and the density of the vapor increases. Evidently at some temperature the two will become identical, and the boundary line between them, *B* (*the meniscus*), will fade out. The temperature at which this occurs is called the *critical temperature*, and the pressure exerted by the vapor is the *critical pressure.* Above this temperature no amount of pressure will liquefy the gas, but will merely compress it. Before any gas can be liquefied it must first be cooled below its critical temperature. The critical points of a few gases are given in the following table:

TABLE OF CRITICAL POINTS

	BOILING POINT	CRITICAL TEMPERATURE	CRITICAL PRESSURE
Hydrogen . .	– 252.7°	– 234.5°	20.0 atmospheres
Nitrogen . . .	– 195.7°	– 146.0°	33.0 atmospheres
Oxygen . . .	– 182.9°	– 119.0°	50.0 atmospheres
Carbon dioxide .	– 78.2°	+ 31.35°	72.9 atmospheres
Water . . .	+ 100.0°	+ 365.0°	194.6 atmospheres

Liquefaction of gases. From what has been said it will be clear that to liquefy a gas the necessary steps are (1) to cool it below its critical temperature, and (2) to apply pressure. At ordinary temperatures many gases are already below their critical temperatures and so can be liquefied by pressure alone.

When the critical temperature is *very low*, as is true with nitrogen and oxygen, the temperature cannot be lowered sufficiently by ordinary cooling, but the cooling is accomplished by mechanical means. Machines constructed for this purpose owe their efficiency to the fact that the heat given out by a gas when it is compressed is not quite so great as that absorbed when it expands. Consequently if the gas is alternately compressed and then allowed to expand, it will grow steadily colder and may presently be cooled below its critical temperature.

The Linde liquid-air machine. The principles just explained are well illustrated in the Linde machine for liquefying air. In the Linde machine (Fig. 41) the compression is effected by a strong pump. The compressed air at 200 atmospheres pressure is first cooled in a freezing bath *A*. It then passes upward as indicated by the arrow and enters the inner tube of a system of three concentric spirally wound copper tubes. At the lower end of this system it expands through a valve operated by the head screw *B* to a pressure of from 20 to 50 atmospheres, and in so doing becomes much colder. It is then returned to the pump through the space between the inner and second tubes and the pipe at the top, cooling the interior, compressed gas. When this process no longer results in a fall of temperature, the valve *C* is opened, whereby some of the cold air at 20 atmospheres pressure is allowed to expand to atmospheric pressure. In so doing a part liquefies and is caught in the vessel *D*, while the very cold air which escapes liquefaction is led back through the outer tube of the spiral to cool further the air within the two inner tubes.

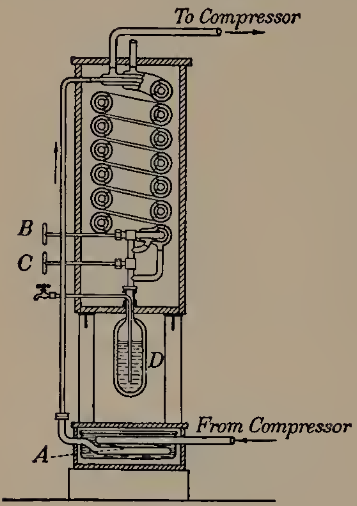


Fig. 41. The Linde machine for liquefying air

Dewar flasks; thermos bottles. Liquid air may be kept for some hours in a special form of flask, devised by the Scottish scientist Dewar, known as a *Dewar flask*. This consists of two concentric vessels (Fig. 42) of any convenient shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent heat conduction. The surface of the outer flask is often silvered in order to reflect the external heat and thus prevent its absorption. The vessels known as *thermos bottles* (Fig. 43) are constructed on the same plan and are very effective for keeping liquids either hot or cold for several hours.

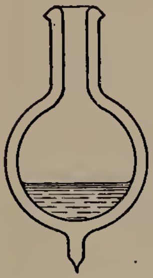


FIG. 42. A Dewar flask for holding liquid air

Solid bodies. When a liquid substance is cooled it becomes less and less fluid. At a sufficiently low temperature all liquids become rigid and we call this form a *solid*. As a rule the change from liquid to solid is sudden. At some definite temperature crystals (p. 112) begin to form and the temperature of the liquid comes to a perfectly definite value called the *freezing point*, and this remains unchanged until all of the liquid has solidified. For example, water solidifies, or freezes, at 0°. Solids formed in this way are always *crystalline*. Less frequently there is no definite point of solidification, the changes from the liquid state into that of a rigid body being very gradual. Glasses, glazes, glue, tar, and gums are examples of such materials. These are sometimes called *amorphous solids* to distinguish them from crystalline solids, but it is better to consider them as still liquid, but so lacking in fluid properties that they are as rigid as crystalline solids.

FIG. 43. A thermos bottle

Freezing point. When a crystallizable liquid, such as water, is cooled, it does not always *begin* to crystallize at its freezing point. Indeed, liquid water has been cooled to −90° without freezing. A liquid below its freezing point is said to be *undercooled.*

If a crystal once forms or one is dropped into the undercooled liquid, solidification at once begins, heat is given out in the process, and the temperature rises to the true freezing point and remains there as long as any liquid is present. The freezing point is best defined as the temperature at which both solid and liquid will remain in contact with each other without change of temperature.

Heat of solidification. The heat given out when 1 g. of a liquid at its freezing point solidifies to 1 g. of solid is called the *heat of solidification.* For water this amounts to 80 cal. If it were not for this liberation of heat, which opposes solidification, ponds would freeze solid in the winter as soon as crystallization had begun. Liquids which do not have definite freezing points have no heat of solidification; this shows that the rigid bodies formed from them are fundamentally different from crystalline solids.

Melting point. If a crystalline solid is slowly heated, its temperature steadily rises to its freezing point and the change to the liquid then begins; and it has not been found possible to heat the solid beyond this point. The melting point and the freezing point are therefore at the same temperature. To convert 1 g. of a solid at its melting point into a liquid at the same temperature absorbs the same quantity of heat as was liberated during solidification. This is called the *heat of fusion.* Amorphous rigid bodies have no definite melting point or heat of fusion.

The manufacture of ice. The manufacture of ice is based on the principle that in the process of vaporizing a liquid a great deal of heat is absorbed (heat of vaporization). If the process is so conducted that the liquid in vaporizing absorbs this heat from water, the temperature of the water may be brought to the freezing point, and by still further absorption of heat the water may be frozen. It will be recalled that for every gram of water at 0° frozen into ice 80 cal. must be absorbed. The liquid chosen to be vaporized must readily pass into a vapor at 0° by lowering the pressure upon it, and it should have as great a heat of vaporization as possible. Liquid ammonia (heat of vaporization, 330 cal.) is the one most frequently used.

The general method used in the manufacture of artificial ice may be understood by reference to Fig. 44. Ammonia, a gaseous compound formed when soft coal is heated in the absence of air (p. 307), is liquefied by means of a compressor pump and led into the pipes *A*, *B*. The heat of condensation is absorbed by water flowing over the pipes. These pipes lead into coils in a large tank nearly filled with brine, prepared by dissolving calcium chloride in water. By means of an expansion valve *C* the pressure upon the liquid ammonia is diminished as it enters the coils, and the heat absorbed by the rapid evaporation of the liquid lowers the temperature of the brine below 0°. Metal vessels *D*, *E*, *F*, filled with pure water, are lowered into the cold brine and left until the water in them is frozen into cakes of ice. The gaseous ammonia is led through *G* back to the compressor pump and again liquefied. In a similar way the temperature is kept low in the cold-storage plants, now so largely used for preserving food products from decay. The rooms of the plant are supplied with pipes, into which liquid ammonia is forced and allowed to vaporize.

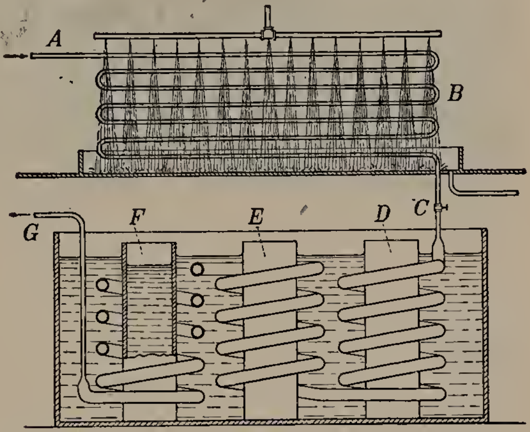


FIG. 44. Diagram illustrating the principle of an ammonia ice machine

Crystals. Crystals may be obtained by cooling melted solids, by the evaporation of solutions, or by cooling the vapors of solids. They are solids bounded by plane surfaces, and these surfaces are arranged in orderly fashion with reference to coördinate lines drawn through the crystal and called the *crystal axes.* Every crystal has therefore a perfectly definite form (Fig. 45). Although there are thousands of these forms, they may all be considered to be modifications of six fundamental forms, referred to six arrangements of axes. A general discussion of these forms will be found in the Appendix.

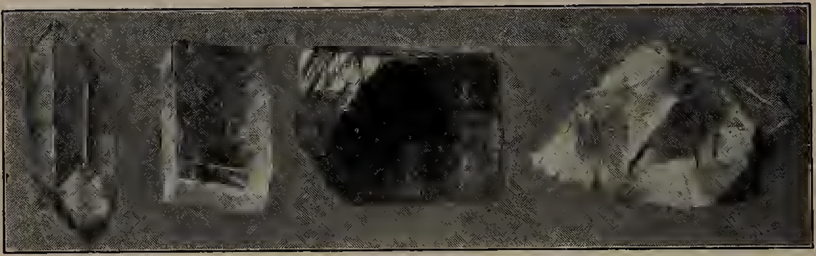


FIG. 45. Some typical examples of crystals

Allotropic forms. Quite a number of the elements are known to exist in two or more forms that are related to each other in such a way that one can be converted into the other by the absorption or liberation of energy. Such modifications of an element are called *allotropic forms.* Graphite and the diamond are two solid allotropic forms of the element carbon (p. 116).

The change of an element into an allotropic modification is very similar to the change of a solid into a liquid or of a liquid into a gas. The heat absorbed corresponds to the heat of fusion or of vaporization, and the form that has the greater energy is the most active chemically, just as steam is more active than water, and water than ice.

One of the most interesting instances of an element existing in two allotropic forms, and the one earliest known, is that of *oxygen and ozone.*

Ozone. As early as 1785 the Dutch chemist Van Marum noticed the peculiar odor that is often observed near an electrical machine when it is discharging sparks through the air. As the result of a great deal of investigation it has been shown that this odor is due to a definite substance called *ozone.* Under ordinary conditions ozone is a pale-blue gas, and when liquefied it is deep-blue in color and boils at – 119°. It can be made from pure oxygen by the action of electrical discharge, and consequently contains no element other than oxygen.

Preparation of ozone. Ozone is most easily prepared by passing a silent electric discharge (or electric waves) through oxygen. This is done in an apparatus represented in Fig. 46. Oxygen enters at *A* and follows the course indicated by the arrows. The metal surfaces *B* and *C* are separated from each other by a space through which the oxygen passes, and are further insulated by the glass *D.* Wires from an induction coil are connected with *B* and *C.* As the oxygen passes upward between the metal plates it is subjected to the electric discharge, and a portion of the oxygen is changed into ozone.

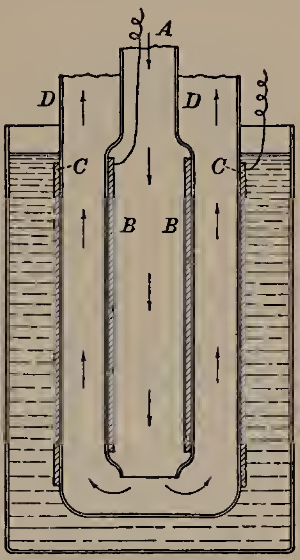


FIG. 46. A convenient form of an apparatus for changing oxygen into ozone

Ozone is also formed in many cases of slow combustion, as when a stick of phosphorus, partly covered with water to keep it from taking fire, is exposed to air (Fig. 47). It is doubtless formed during lightning discharges, but it is doubtful whether any of it is normally present in air, for it is very easily decomposed into ordinary oxygen.

Conduct and uses of ozone. Ozone resembles oxygen in many respects, but it is very much more active. Consequently it is a powerful oxidizing agent. It acts upon many colored substances (dyes), converting them into colorless compounds, and on this account is used to bleach many substances, such as waxes and oils. It destroys many low forms of life and is used as a disinfectant and for purifying water for drinking supplies.

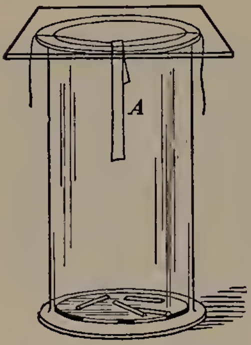


Fig. 47. Formation of ozone by the action of moist air on phosphorus

The energy of ozone. Ozone is made from oxygen under conditions that add energy to the oxygen. This energy is stored up in the ozone as chemical energy and is available when ozone acts upon other substances. It will later be shown that the molecule of ozone consists of three oxygen atoms, while that of oxygen consists of but two. Ozone therefore differs from oxygen (1) in chemical energy and (2) in molecular structure. The conversion of oxygen into ozone may be represented in the equation

$$3\,O_2 + (3 \times 21{,}500 \text{ cal.}) \longrightarrow 2\,O_3$$

EXERCISES

1. What are the conditions which determine the physical state of any element? Illustrate in the case of oxygen.

2. Can all solid substances be melted without decomposition? Illustrate by an example.

3. Can all liquids be boiled without decomposition? Illustrate by an example.

4. When a pond begins to freeze in winter, why does not all the water freeze?

5. Why does a block of ice melt so slowly even in warm air?

6. What becomes of the heat applied to a boiling liquid?

7. Why is it necessary to boil eggs longer on a mountain top than at the seashore in order to cook them?

8. Name three crystalline substances.

9. How can you crystallize common salt?

10. Tubs of water are sometimes placed in cellars, in order to prevent the freezing of the stored fruits and vegetables. Is this practice based on scientific grounds?

11. Suppose ice and water to be mixed together at 0°. Under what conditions will more water freeze? more ice melt?

12. Suggest a method of raising the boiling point of water above 100°.

13. When water freezes in a bottle, why is the bottle broken? Would all other liquids act in the same way?

14. How many calories of heat are given off in the freezing of 500 g. of water at 0°?

15. How many calories are required to change 1 kg. of ice at 0° to water at 70°?

16. How many calories are required to change 1 kg. of water at the temperature of your room into steam at 100°?

17. What weight of ice could be melted by the heat evolved in the condensation of 50 lb. of steam at 100° to water at the same temperature? (1 lb. = 453.6 g.)

18. 100 lb. of ice at 0° was placed in a refrigerator. The water resulting from the melted ice absorbed sufficient heat to raise its temperature to 8° before it flowed from the refrigerator. Calculate the total number of calories of heat absorbed by the ice and the resulting water.

CHAPTER X

CARBON AND CARBON DIOXIDE

Introduction. Carbon is one of the most familiar of the elements, being present in coal and charcoal in the free state. Its most common oxide, called carbon dioxide, is formed in the processes of respiration and combustion, and is of great importance. It is therefore desirable that we should learn something of the properties and chemical conduct of these two substances at an early stage in our study.

Occurrence of carbon. In the uncombined state carbon is found in nature in several forms. The diamond is virtually pure carbon, while graphite and the different varieties of coal all contain more or less free carbon. The element also occurs abundantly in the form of compounds. Carbon dioxide is its most familiar gaseous compound. Natural gas and petroleum are largely compounds of carbon and hydrogen. The carbonates, especially calcium carbonate (limestone), constitute great strata of rocks, and are found in almost every locality. All living organisms, both plant and animal, contain a large percentage of this element, and the number of its compounds which help to make up the great variety of animate nature is almost limitless. In the free state carbon occurs in both the crystalline and the amorphous form.

Crystalline carbon. Crystalline carbon occurs in two forms, — the diamond and graphite.

1. ***Diamond.*** Diamonds are found in certain localities in South Africa, the East Indies, and Brazil. The crystals as found are usually covered with a rough coating. These are cut so as to bring out the brilliancy of the gem. Diamond cutting is carried on most extensively in Holland.

Fig. 48. The Cullinan diamond in its original condition (one half natural size)

The weight of the diamond is usually expressed in carats, a carat being equal to about 0.2 g. The word *carat* is derived from a Greek word meaning "the seed, or bean, of the carob, or locust, tree." The beans were formerly used in weighing diamonds.

The largest diamond known was found in the Transvaal mines in 1905, and weighed $3025\frac{3}{4}$ carats. This was called the Cullinan diamond (Fig. 48) and was presented to King Edward VII by the Transvaal government. It was subsequently cut into nine large stones and a number of smaller ones. The two largest of these weigh 516.5 and $309\frac{3}{16}$ carats and are the largest cut diamonds in existence. Other famous diamonds are the Kohinoor ($106\frac{1}{4}$ carats) (Fig. 49), the Nizam (277 carats), the Victoria (180 carats), and the Jubilee (239 carats).

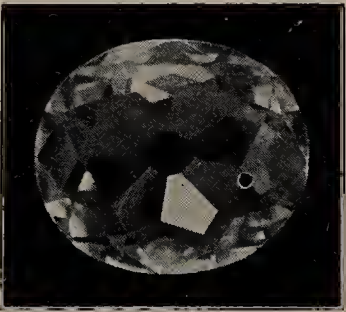


Fig. 49. The Kohinoor diamond after being cut (natural size)

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it, but when heated in oxygen or the air, it blackens and burns, forming carbon dioxide.

Artificial production of diamonds. Many attempts have been made to produce diamonds artificially. For a long time these ended in failure, graphite and not diamonds being the product obtained, but in 1893 the French chemist Moissan (Fig. 103), in his study of chemistry at high temperatures, finally succeeded in making some small ones. He accomplished this by dissolving carbon in melted iron and plunging the crucible containing the solution into water, as shown in Fig. 50. Under these conditions the carbon crystallized in the iron in the form of the diamond. The diamonds were then freed from the metal by dissolving away the iron in hydrochloric acid.

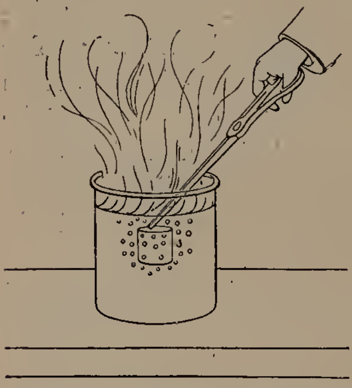


FIG. 50. Sketch illustrating the method of producing diamonds in the laboratory

2. ***Graphite.*** This form of carbon is found in large quantities, especially in Ceylon, Siberia, and in some parts of the United States and Canada. Large quantities are also made commercially by heating hard coal to a high temperature. It is a glistening black substance, very soft, and greasy to the touch. Its density is about 2.15. It is used in the manufacture of lead pencils and crucibles, as a lubricant, and, in the form of a polish or a paint, as a protective covering for iron.

Commercial production of graphite. The process consists in heating hard coal in large electric furnaces about 40 ft. in length, a longitudinal section of one of which is shown in Fig. 51. The electrodes *A* are made of graphite. The furnace is nearly filled with the coarse grains of coal (*B*). Since the coal is a poor conductor, there is placed in the center of the charge a core (*C*) of carbon, which serves to conduct the current through the charge. The charge is covered with a mixture (*D*) of sand

and carbon (or similar materials), which excludes the air. An alternating current is supplied by the generator *G*. Under the influence of the intense heat produced by the current, the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit, and is therefore superior to the natural product.

Amorphous carbon. Pure amorphous carbon is best prepared by heating sugar ($C_{12}H_{22}O_{11}$) in the absence of air. The hydrogen and oxygen present are expelled, largely in the form of water, and pure carbon remains. Among the numerous substances that contain amorphous carbon, the following may be mentioned:

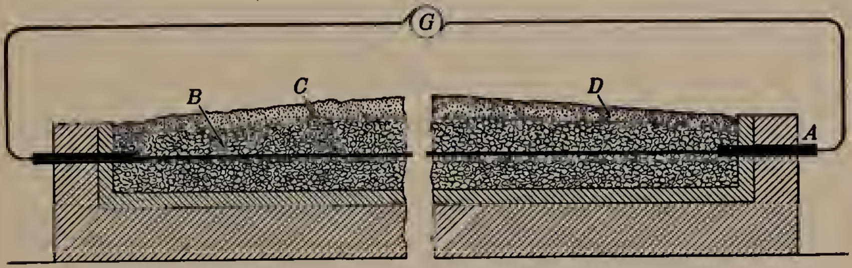


FIG. 51. Electric furnace for the production of graphite

1. ***Coal and coke.*** The various forms of coal were formed from vast accumulations of vegetable matter. In hard, or anthracite, coal nearly all of the carbon is in the uncombined state; while in soft, or bituminous, coal a considerable portion of the carbon is combined with hydrogen, oxygen, nitrogen, and sulfur. When soft coal is heated in the absence of air (p. 306) complex changes occur, resulting in the formation of various useful compounds of carbon, which are given off in the form of gases and vapors, while the mineral matter and free carbon remain and constitute ordinary *coke*. The matter which escapes when coal is heated in the absence of air is known as

volatile matter. In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left in the form of *ash.*

2. ***Charcoal.*** This is prepared from wood just as coke is prepared from coal. The volatile matter expelled consists of many valuable substances, such as wood alcohol and acetic acid, which are obtained commercially in this way. Formerly much of this volatile matter was allowed to escape, but at present an increasing amount of charcoal is prepared in such a way that the volatile matter is condensed and saved. Both charcoal and coke are used as fuels, and they are especially useful in reducing metals from their oxides, as will be described later.

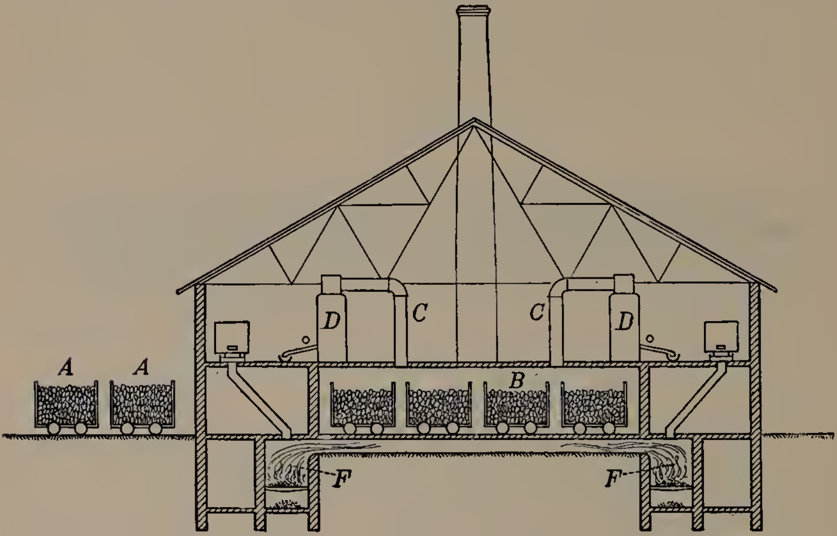


FIG. 52. The modern method for the production of charcoal

Modern methods for the production of charcoal. Iron cars are loaded with wood, *A*, *A* (Fig. 52), and run into the retort *B*. The retort is then made air-tight and heated slowly for twenty-four hours by the fires *F*, *F*. The gaseous products escape through the pipes *C*, *C* and then pass into the condensers *D*, *D*. Here those portions which are liquid at ordinary temperatures, such as wood alcohol and acetic acid, are condensed, while the gaseous products are led back into the furnace and burned. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood.

3. ***Bone black, or animal charcoal.*** This is made by charring bones and animal refuse. It consists of very finely divided carbon and of calcium phosphate, and is especially useful for removing coloring matter in the refining of sugar.

4. ***Carbon black; lampblack.*** These are products of the imperfect combustion of gas and oil.

Destructive distillation. The process of decomposing such substances as coal, wood, and bones by heating them in the absence of air is termed *destructive distillation.* Thus, we say that coke, charcoal, and bone black are made by the destructive distillation of coal, wood, and bones, respectively.

Properties of carbon. While the various forms of carbon differ in many properties, especially in color and hardness, yet they are all odorless, tasteless solids, insoluble in water. Only in the intense heat of the electric arc does carbon volatilize, passing directly from the solid state into a vapor without melting. Owing to this fact, the inside surface of an incandescent-light bulb after being used for some time becomes coated with a dark film of carbon. In the form of bone black, or charcoal, carbon has the property of absorbing relatively large volumes of certain gases, as well as many kinds of organic matter, from their solutions. As a result of this property, filtration through a charcoal filter will often remove objectionable odors and colors from solutions.

Chemical conduct. At ordinary temperatures carbon is a very inactive substance, but at higher temperatures it combines directly with a number of elements, such as oxygen, hydrogen, and sulfur. Because of its strong affinity for oxygen at high temperatures it is an excellent reducing agent. Carbon also combines directly with many of the metals, forming compounds called *carbides.* One of the most important of these is calcium carbide (CaC_2), used so largely in the preparation of acetylene and fertilizers. When heated in the presence of sufficient oxygen, carbon burns, forming carbon dioxide.

Uses of carbon. The chief use of amorphous carbon is for fuel, to furnish heat and power for all the uses of civilization. An enormous quantity of carbon, in the form of coal, coke, and charcoal, is used as a reducing agent in the separation of the various metals from their ores. Carbon black is used for making rubber tires, printer's ink, paints, and black varnishes, while bone black and charcoal are used in water filters. In the refining of sugar the dark solution of the impure compound is filtered through bone black, which removes the coloring matter. On evaporation the resulting solution yields the colorless sugar.

Carbon dioxide (CO_2). Carbon dioxide is a colorless gas which is formed whenever carbon burns in an atmosphere containing oxygen. Since all of the common fuels, such as coal, wood, oil, and gas, contain carbon either in a free or in a combined state, it follows that carbon dioxide is formed whenever these fuels are burned. The gas is also formed in the process of respiration, from 4 to 5 per cent of it being present in exhaled air. It is likewise formed in the processes of fermentation which take place in the manufacture of alcohol and of alcoholic liquors, as well as in making lime by heating limestone (p. 425). Large quantities of it escape from volcanoes and from crevices in the earth. It is present in the air to the extent of about 3 parts in 10,000, and this apparently small quantity is of fundamental importance in nature, as will be pointed out in describing the atmosphere.

Preparation. In the laboratory, carbon dioxide is prepared by the action of hydrochloric acid on the compound known as calcium carbonate ($CaCO_3$). The latter is found in nature in many different substances, such as shells, coral, and limestone. Marble is nearly pure calcium carbonate, and, being comparatively inexpensive, is the material most often used in the preparation of carbon dioxide. When hydrochloric acid and marble are brought in contact with each other, water, calcium chloride ($CaCl_2$), and carbon dioxide are formed according to the following equation:

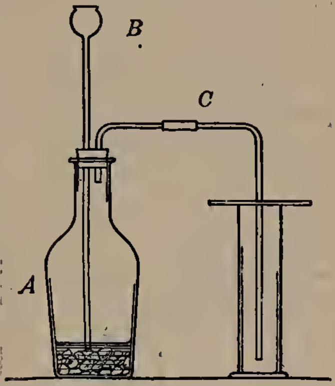


FIG. 53. A simple apparatus for preparing carbon dioxide

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

The calcium chloride is a white solid which remains in solution, while the insoluble carbon dioxide escapes and is collected by the displacement of air as described below.

The gas may be prepared in the apparatus shown in Fig. 53. Pieces of marble are placed in flask *A*, and hydrochloric acid diluted with an equal volume of water is slowly added through the funnel tube *B*. The tube *C*, through which the carbon dioxide escapes as fast as formed, passes through a piece of cardboard placed over the mouth of a bottle or cylinder as shown in the figure. The gas is heavier than air and gradually fills the cylinder, pushing out the air. A lighted splint brought into the mouth of the cylinder is extinguished when the cylinder is filled with the gas.

The Kipp apparatus (Fig. 17) is more convenient than that shown in Fig. 53. It is used as in the preparation of hydrogen, marble being substituted for the zinc.

Properties. Carbon dioxide is a colorless, almost odorless gas, one liter of which weighs about 1.5 times as much as one liter of air. It can be poured like water from one vessel downward into another; or as a more striking experiment the gas may be poured from a cylinder *A* into a beaker *B*, attached to a balance and counterpoised as shown in Fig. 54. At 15° and under ordinary pressure 1 volume of water dissolves 1 volume of the gas. It is rather easily condensed to a white solid which, under ordinary pressure, evaporates without melting at – 78.2°.

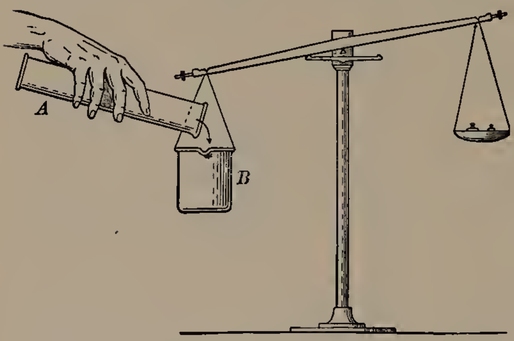


Fig. 54. A method for showing the weight of gaseous carbon dioxide

Liquid and solid carbon dioxide. Carbon dioxide may be purchased condensed in strong steel cylinders. In these cylinders the compound is under such great pressure that it is largely in the liquid state. When the pressure is removed, the rapid vaporization of the liquid lowers the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid. Cylinders of liquid carbon dioxide are inexpensive and should be available in every school. The commercial supply of this gas is obtained largely from fermentation processes, especially from breweries.

To prepare the solid carbon dioxide, the cylinder should be placed across the table and supported in such a way that the stopcock end is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth around the neck of the stopcock. The stopcock is then turned on so that the liquid rushes out in large quantities. Very quickly a considerable quantity of the snow collects in the cloth. Mercury may be frozen by this snow in the following way: A filter paper is placed in the bottom of a small evaporating dish and some mercury poured upon it. One end of a piece of wire is wound into a flat coil and dipped into the mercury. A quantity of the solid carbon dioxide is placed upon the mercury and from 10 to 15 cc. of ether poured over it. The temperature is reduced to $-50°$, so that the mercury solidifies in a minute or two and may be removed from the dish by the wire which serves as a handle.

Chemical conduct. Carbon dioxide is a very stable substance. It is neither combustible nor a supporter of combustion. When it is passed into a clear solution of calcium hydroxide, $Ca(OH)_2$ (ordinary limewater), the solution soon becomes cloudy, owing to the formation of calcium carbonate. This substance is insoluble and separates out as fast as it is formed, producing a cloudy or milky appearance in the solution:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

These properties constitute a simple test for carbon dioxide.

Uses. The carbon dioxide in the air is a food for plants, as will be shown in the chapter on the atmosphere. Commercially it is used chiefly in the manufacture of soda water and similar beverages and as a fire extinguisher. Ordinary soda water consists of different flavoring extracts to which is added water charged with carbon dioxide under pressure. When the pressure is removed, the excess of gas escapes, producing *effervescence.* Most of the portable fire extinguishers are simply devices for generating carbon dioxide. It is not necessary that all the oxygen should be kept away from a fire in order to smother it. A burning candle, for example, is extinguished in air which contains only 2.5 per cent of carbon dioxide.

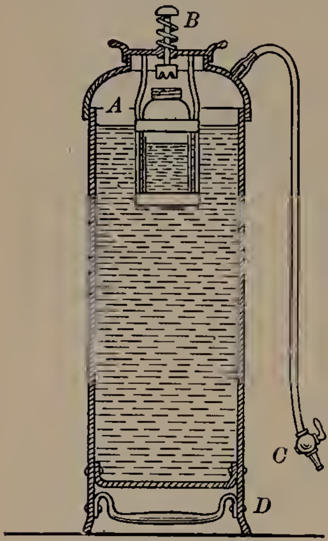


FIG. 55. An example of a modern fire extinguisher

Fire extinguishers. The general type of the portable fire extinguisher is shown in Fig. 55. The liquid is a solution of sodium hydrogen carbonate in water. The bottle *A* contains sulfuric acid in sufficient amount to react with the sodium carbonate in solution. In case of fire, the extinguisher is caught by the handle *D* and inverted, and the bottle containing the sulfuric acid is broken by striking the rod *B* against the floor. The sulfuric acid immediately reacts with the carbonate, generating carbon dioxide, some of which dissolves in the water, while the remainder forces the solution out through the nozzle *C*. While the total quantity of water furnished by such an extinguisher is comparatively small, it is very effective as a fire extinguisher, because of the large percentage of carbon dioxide which it contains in solution.

EXERCISES

1. Suggest a method for proving that all the various forms of carbon described are really carbon.

2. How could you judge of the relative purity of different forms of carbon?

3. How could one distinguish between oxygen, hydrogen, and carbon dioxide?

4. Suggest a method for determining the percentage of carbon in a sample of coal.

5. Apart from its color, why should carbon be useful in the preparation of inks and paints?

6. Report important events in the life of Moissan (consult encyclopedia).

7. (*a*) Calculate the weight of 100 l. of carbon dioxide. (*b*) What weight of marble is necessary for the preparation of this volume of the gas? (*c*) What weight of calcium chloride would be formed in this process?

8. Contrast the boiling points of carbon dioxide, oxygen, and hydrogen.

9. What effect would doubling the pressure have upon the solubility of carbon dioxide in water?

10. Enumerate the important products resulting from the destructive distillation of wood.

11. Why does soda water effervesce?

12. The reaction which takes place when the sulfuric acid and sodium hydrogen carbonate in a fire extinguisher are brought together is represented by the following equation:

$$2\,NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,H_2O + 2\,CO_2$$

(*a*) What weight of hydrogen sulfate would have to be used for each kilogram of the carbonate dissolved in the water? (*b*) What volume of carbon dioxide would be evolved?

13. How could you prove that carbon dioxide is a product of combustion (p. 3)?

14. How could you convert the carbon dioxide in the air which you exhale, into calcium carbonate?

15. What weight of calcium carbonate would be necessary to prepare sufficient carbon dioxide to saturate 10 l. of water at 15° and under ordinary pressure?

16. Suppose the Kohinoor diamond were to be burned in oxygen, calculate the volume of the product of combustion.

CHAPTER XI

NITROGEN AND THE RARE ELEMENTS IN THE ATMOSPHERE

Historical. Nitrogen was discovered by the Scottish chemist Rutherford in 1772. A little later Scheele (Fig. 56) showed it to be a constituent of air, and Lavoisier gave it the name *azote*, signifying that it would not support life. The name *nitrogen* was afterwards suggested because of its presence in saltpeter, or niter. The term *azote* and the symbol Az are still used by the French chemists.

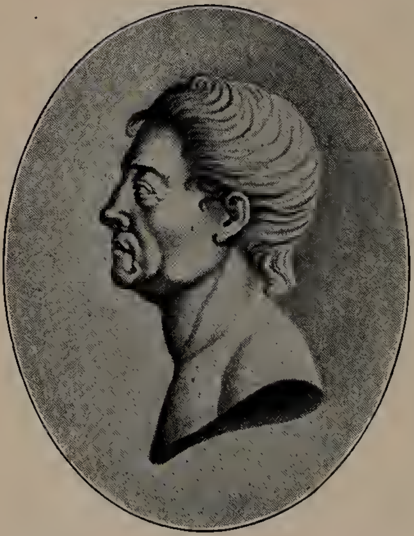


FIG. 56. Karl Wilhelm Scheele (1735–1784)

A Swedish chemist who made many discoveries in chemistry

Occurrence. Air is composed principally of oxygen and nitrogen, each in the free state — about 78 parts by volume out of every 100 parts being nitrogen. Nitrogen also occurs in nature in potassium nitrate (KNO_3) — commonly called saltpeter or niter — as well as in sodium nitrate ($NaNO_3$) (Fig. 163). Nitrogen is also an essential constituent of all living organisms; for example, the human body contains about 3 per cent of nitrogen.

Preparation from air. Nitrogen can be prepared from air by the action of some substance which will combine with the oxygen, leaving the nitrogen free. Such a substance must be chosen, however, as will combine with the oxygen to form a product which is not a gas and which can be readily separated from the nitrogen. The substances most often used for this purpose are phosphorus and copper.

1. *By the action of phosphorus.* The method used for the preparation of nitrogen by the use of phosphorus is as follows:

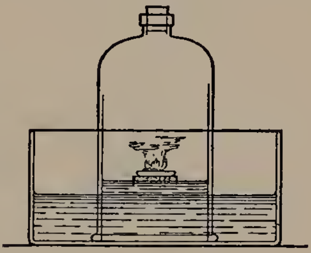


FIG. 57. Preparing nitrogen by burning out the oxygen of air with phosphorus

The phosphorus is placed in a little porcelain dish supported on a cork and floated on water (Fig. 57). It is then ignited by contact with a hot wire, and immediately a bell jar or bottle is brought over it so as to confine a portion of the air. The phosphorus combines with the oxygen to form an oxide of phosphorus known as phosphorus pentoxide. This is a white solid which floats about in the bell jar, but which in a short time is all absorbed by the water, leaving the nitrogen. The withdrawal of the oxygen is indicated by the rising of the water in the bell jar.

2. *By the action of copper.* The oxygen in the air may also be removed by passing air slowly through a heated tube containing copper. The copper combines with the oxygen to form copper oxide, which is a solid. The nitrogen passes on and may be collected over water. The details of the process are as follows:

The copper is placed in a tube *A* (Fig. 58) and heated. Air is then forced slowly through the tube by pouring water into the bottle *B*. The oxygen of the air combines with the hot copper, forming the black solid, copper oxide (CuO), which remains in the tube, while the nitrogen passes on and is collected over water in the cylinder *C*.

The nitrogen obtained from air by the above methods is never quite pure, but contains about 1 per cent of a mixture of other gases (p. 133). The properties of the nitrogen, however, are not materially affected by the presence of these gases. If we wish to obtain pure nitrogen, we may do so by heating certain compounds of nitrogen.

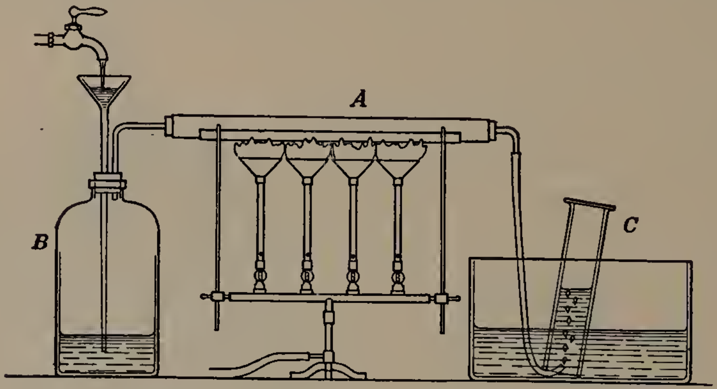


FIG. 58. Preparing nitrogen by removing the oxygen from air with hot copper

Preparation from compounds of nitrogen. The compound most often used for the preparation of nitrogen is ammonium nitrite (NH_4NO_2). When heated, this compound decomposes into nitrogen and water, as represented in the following equation:

$$NH_4NO_2 \longrightarrow N_2 + 2\,H_2O$$

Since ammonium nitrite is not readily kept in the pure state, it is convenient to substitute for it a mixture of sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl). These two compounds react to form sodium chloride and ammonium nitrite:

$$NaNO_2 + NH_4Cl \longrightarrow NH_4NO_2 + NaCl$$

Commercial methods of preparation. It is evident that the method used for the preparation of oxygen from liquid air (p. 28) would serve equally well for the preparation of nitrogen. This method has come to the front during the World War through the development of more efficient machines for liquefying air (p. 108). By this method is prepared the large amount of nitrogen used in the manufacture of ammonia by the Haber Process (p. 203) as well as of certain fertilizers.

Properties. Nitrogen, like hydrogen and oxygen, is a colorless, odorless, tasteless gas. It is slightly lighter than oxygen, 1 l. of it weighing 1.2507 g. Its solubility in water is about the same as that of hydrogen, 1 l. of water dissolving about 20 cc. of the gas under standard conditions. Liquid nitrogen is colorless, boils at −195.7°, and has a density of 0.8 at its boiling point. At a still lower temperature it may be obtained in the form of an icelike solid melting at −210.5°.

Chemical conduct. Nitrogen is much less active than oxygen, showing little or no tendency to combine with any other elements at ordinary temperatures. At higher temperatures it combines with magnesium, lithium, titanium, and a number of other elements. The compounds formed are in general called *nitrides*, just as compounds of an element with oxygen are called *oxides*. When nitrogen is mixed with oxygen and subjected to the action of electric sparks, the two gases slowly combine, and form oxides of nitrogen. A mixture of nitrogen and hydrogen when treated similarly forms ammonia (NH_3), a gaseous compound of nitrogen and hydrogen. Since we are constantly inhaling nitrogen, it is evident that it is not poisonous. Nevertheless life would be impossible in an atmosphere of pure nitrogen on account of the exclusion of the necessary oxygen.

The assimilation of nitrogen by plants. While nitrogen is an essential constituent of both plants and animals, yet, with the exception of a few plants, especially those belonging to the natural order *Leguminosae*, these organisms have not the power of directly assimilating free nitrogen from the atmosphere, but obtain their supply from certain compounds of nitrogen. It has long been known that some of the leguminous plants, such as the beans, peas, and clover, not only thrive in poor soil but at the same time enrich it. Investigation has shown that these plants obtain at least a portion of their supply of nitrogen from the atmosphere. The assimilation of nitrogen is accomplished through the agency of groups of microörganisms which produce little tubercles on the roots of the plants, as represented in Fig. 59. The figure shows the tubercles on the roots of a variety of bean. These microörganisms have the power of converting free nitrogen taken from the air into compounds of nitrogen, some of which are assimilated by the plant, while others are left in the soil and thus enrich it.

FIG. 59. Tubercles on the roots of bean plants

Uses of nitrogen. Free nitrogen is used to a limited extent in the preparation of certain nitrogenous compounds (p. 462) employed as fertilizers. Mercurial thermometers designed for use at temperatures of from 300° to 500° are filled (over the mercury) with nitrogen under pressure. In this way the mercury is prevented from boiling, even at temperatures considerably above its ordinary boiling point (357°).

Argon, helium, neon, krypton, xenon. These are rare elements and occur in the air in very small quantities. They are similar in that they are all colorless, odorless gases. They differ from all other known elements in that they are entirely inert, forming no compounds whatever. Argon, the most abundant of the group, was discovered in 1894 by two British scientists, Lord Rayleigh and Sir William Ramsay (Fig. 60). In 1868 Lockyer showed that a gaseous element, to which he gave the name *helium*, was present in the gases surrounding the sun. In 1895 Ramsay showed that this same element was present in the gases evolved in heating certain minerals, and later that traces of it were present in the atmosphere. The three remaining members of the group were discovered in liquid air by Ramsay and Travers in 1898.

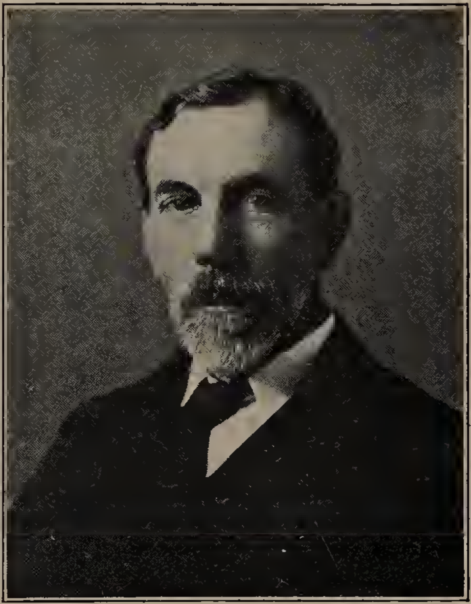


Fig. 60. Sir William Ramsay (1852–1916)

Famous for his discovery of the rare gases in the atmosphere and for his researches in radioactivity

The commercial preparation of helium. Helium is also present to the extent of nearly 1 per cent in the natural gas found in certain localities, especially in Kansas and Texas. When the United States entered the war, experimental plants were built in Texas for the purpose of developing, if possible, a commercial method for the separation of the helium present in natural gas, in the hope that the element could be obtained in sufficient quantities to allow its use as a material for filling balloons and dirigibles; for, while helium is not so light as hydrogen, it possesses a very great advantage over hydrogen, as a material for filling balloons, in being noninflammable. These experiments were successful, and, had the war continued a few months longer, an adequate supply would have been at hand. The method used for the separation of helium was similar to that used in the preparation of oxygen and nitrogen from liquid air, advantage being taken of the fact that helium has a very low boiling point, namely, – 268.7°.

Some facts pertaining to the rare gases in the atmosphere are given in the following table:

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 l. of gas .	0.1782 g.	0.9002 g.	1.7809 g.	3.708 g.	5.851 g.
Boiling point of liquid	– 268.7°	– 239°	– 186°	– 151.7°	– 109°
Number of volumes in 1,000,000 volumes of air (approximate) .	4.00	12.3	9400	0.05	0.006

EXERCISES

1. How could you distinguish between oxygen, hydrogen, and nitrogen?

2. Calculate the relative weights of nitrogen and oxygen; of nitrogen and hydrogen.

3. In the preparation of nitrogen from the air, how would hydrogen do as a substance for the removal of the oxygen?

4. Why not prepare nitrogen by burning a candle in confined air?

5. Which contains the greater percentage of nitrogen, sodium nitrate or potassium nitrate?

6. What is the significance of each of the following names: argon, helium, neon, krypton, xenon? (Consult dictionary.)

7. Note some of the important discoveries made by Scheele (consult encyclopedia).

8. What weight of nitrogen can be obtained from 10 l. of air measured under the conditions of temperature and pressure which prevail in your laboratory?

CHAPTER XII

THE ATMOSPHERE

Historical. The terms *atmosphere* and *air* are often used interchangeably, although strictly speaking the former term is applied to the entire gaseous envelope surrounding the earth, while the latter is applied to a limited portion of this envelope. Like water, air was formerly regarded as an element. Near the close of the eighteenth century, however, through the experiments of Scheele, Priestley, Cavendish, and Lavoisier, it was shown to be a mixture of at least two gases, — those which we now call oxygen and nitrogen. By absorbing the oxygen from an inclosed volume of air and measuring the contraction in volume caused by the removal of oxygen, Cavendish was able to determine with considerable accuracy the relative volumes of oxygen and nitrogen.

Composition of the air. The normal constituents of air, together with the approximate volumes of each in samples collected in the open fields, are as follows:

Oxygen	21 volumes in 100 volumes of dry air
Nitrogen	78 volumes in 100 volumes of dry air
Water vapor	variable within wide limits
Carbon dioxide . . .	3 to 4 volumes in 10,000 volumes of dry air
Argon	0.940 volumes in 100 volumes of dry air
Helium, neon, krypton, xenon	traces

In addition, there are usually present small quantities of hydrogen peroxide, oxides of nitrogen, ammonium nitrate, microörganisms, dust particles, and traces of hydrogen. The air in large cities and manufacturing districts is also likely to contain certain gases evolved in manufacturing processes. Among these are hydrogen sulfide (H_2S) and sulfur dioxide (SO_2).

Water vapor in the air. The quantity of water vapor which may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cu. m. of air can absorb at the temperature indicated:

Temperature,	0°	10°	20°	30°
Weight of water,	4.8 g.	9.9 g.	17.1 g.	30 g.

The constituents of the air that are essential to life. The constituents that are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide.

The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. It is likewise assimilated by certain plants (p. 132). The water vapor prevents excessive evaporation of the water present in organisms, while the carbon dioxide is an essential plant food.

The quantitative analysis of air. A number of different methods have been devised for the determination of the percentages of the constituents of the atmosphere. Among these are the following:

1. ***Determination of oxygen.*** The oxygen is withdrawn, by means of phosphorus, from a measured volume of air inclosed in a tube.

To make the determination, a graduated tube is filled with water and inverted in a vessel of water. A sample of the air to be analyzed is then introduced into the tube until the tube is nearly filled with the gas, and the volume is carefully noted. A small piece of phosphorus is attached to a wire and brought within the tube as shown in Fig. 61. After a few hours the oxygen in the inclosed air will have combined with the phosphorus, the water rising to take its place. The phosphorus is removed, and the volume is again noted. The contraction in the volume of the air is equal to the volume of oxygen absorbed from the air.

2. ***Determination of nitrogen.*** If the gas left after the removal of oxygen from a portion of air is passed over heated magnesium or lithium, the nitrogen present in the gas is withdrawn, leaving argon and the other rare elements. It may thus be shown that, of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of dry air, approximately 78 volumes are nitrogen and 0.94 argon. The other elements are present in such small quantities that they may be neglected.

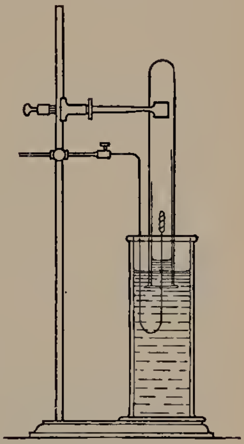


FIG. 61. The determination of the oxygen in air by means of phosphorus

3. ***Determination of water vapor and carbon dioxide.*** These constituents are determined by passing a known volume of air through two tubes, the first containing calcium chloride, and the second calcium hydroxide, or, better, sodium hydroxide. The calcium chloride removes the moisture, while the sodium hydroxide removes the carbon dioxide. The increase in the weights of these two substances will give the weights of moisture and carbon dioxide respectively in the original volume of air.

Processes tending to change the composition of the air. These processes fall into two classes: those which increase the carbon dioxide and those which diminish it.

1. ***Processes tending to increase the quantity of carbon dioxide.*** Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes and crevices in the earth's crust, but certain processes are constantly taking place which are attended by evolution of this gas. Chief among these are the following: (a) *Respiration.* In this process some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon present in the tissues of the body, the reaction being attended by a transformation of chemical energy into heat and muscular energy. The products of oxidation are carried back to the lungs and exhaled largely in the form of carbon dioxide. (b) *Combustion.* All the ordinary fuels contain large percentages of carbon. On burning, this is oxidized to carbon dioxide. (c) *Decay of organic matter.* When organic matter decays in the air the carbon present is oxidized to carbon dioxide.

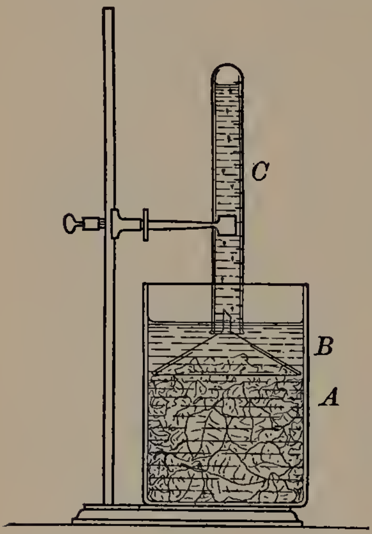


Fig. 62. The liberation of oxygen from plants exposed to sunlight

2. ***Processes tending to decrease the quantity of carbon dioxide.*** There are two general processes which tend to diminish the quantity of carbon dioxide in the atmosphere.

(a) *The action of plants.* Plants have the power, when growing in sunlight, of absorbing carbon dioxide from the air, retaining the carbon and returning a portion of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

That plants evolve oxygen in the sunlight may be shown as follows: Some freshly gathered leaves are placed under water in the jar *A* (Fig. 62) and covered with the funnel *B*, the stem of which extends into the graduated tube *C*. Bubbles of oxygen make their escape from the surface of the leaves and may be collected in the measuring tube *C*.

(b) *The weathering of rocks.* Large quantities of carbon dioxide are being constantly withdrawn from the atmosphere through its combination with various rock materials.

The composition of the air constant. Notwithstanding the changes taking place which tend to alter the composition of the air, the results of the analyses of air show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant. Indeed, so constant are the percentages of oxygen and nitrogen that the question has arisen, whether air is not a definite chemical compound.

Air a mixture. That the oxygen and nitrogen in the air are not combined may be shown in a number of ways, among which are the following:

1. When air dissolves in water it has been found that the ratio of oxygen to nitrogen in the dissolved air is no longer 21 : 78, but more nearly 35 : 65. If air were a chemical compound, the ratio of oxygen to nitrogen would not be changed by solution in water.

2. A chemical compound in the form of a liquid has a definite boiling point at a given pressure (p. 105). Water, for example, boils at 100° under standard pressure. Moreover, the steam which is formed has the same composition as the water. The boiling point of liquid air, on the other hand, gradually rises as the liquid boils, the nitrogen escaping first, then the oxygen. If the two were combined, they would pass off together in the ratio in which they are found in the air.

Why the air has a constant composition. If air is a mixture and changes are constantly taking place which tend to modify its composition, how, then, do we account for the constancy of composition which the analyses reveal? This is explained by several facts: (1) The changes which are caused by the processes of combustion, respiration, and decay, on the one hand, and the action of plants, on the other, tend to equalize each other. (2) The winds keep the air in constant motion and so prevent local changes. (3) The volume of air is so vast and the changes which occur are so small, compared with the total volume, that they cannot be readily detected. (4) Finally, it must be noted that only air collected in the open fields shows this constancy in composition. The air in a poorly ventilated room occupied by a number of people rapidly changes in composition.

Impure air and ventilation. The difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air are shown in the following table:

Constituent	Inhaled air	Exhaled air
Oxygen	21.00%	16.00%
Carbon dioxide	0.04%	4.38%
Water vapor	variable	saturated

The injurious effects resulting from inadequate ventilation seem to be due neither to lack of oxygen nor to the excess of carbon dioxide; rather they are due to high temperature and to the presence of an abnormal amount of water vapor, both of which conditions are apt to prevail in crowded and poorly ventilated rooms.

Not only is water vapor exhaled from the lungs, but there is constant evaporation of moisture from the pores of the skin, and in this process much heat is absorbed. Notwithstanding the extreme changes in the temperature of the air, the temperature of the body in health remains nearly constant. It is partly by variations in the amount of moisture evaporating from the skin that the temperature of the body is maintained at this constant value. If an abnormal amount of water vapor is present in the air, the evaporation of moisture from the skin takes place very slowly, and bodily discomfort follows. Moreover, when the air is perfectly still, that portion of the air in contact with the body tends to become saturated with moisture, and evaporation diminishes; hence the relief that comes from keeping the air in motion, as with an electric fan.

In general, a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but in general may be said to be about 30 cu. ft. per minute for each person.

The properties of air. Inasmuch as air is composed principally of a mixture of oxygen and nitrogen, which elements have already been discussed, its properties may be inferred largely from those of the two gases. One liter weighs 1.2928 g.

Liquid air. We have seen (p. 108) that air, like all other gases, can be liquefied by the combined effect of pressure and low temperature. Liquid air is essentially a mixture of liquid nitrogen (boiling point, – 195.7°) and liquid oxygen (boiling point, – 182.9°); hence if liquid air is allowed to evaporate, the nitrogen tends to vaporize first. Advantage is taken of this difference in boiling points to separate the oxygen and nitrogen from each other, and the method serves as a commercial one for obtaining the two gases. Liquid air is also employed when very low temperatures are desired. It may be kept for several hours by storing it in Dewar flasks (Fig. 42).

The extremely low temperature of liquid air may be inferred from the fact that mercury when cooled by it is frozen to a mass so hard that it may be used for driving nails.

EXERCISES

1. When oxygen and nitrogen are mixed in the proportion in which they exist in the atmosphere, heat is neither evolved nor absorbed by the process. What important point does this suggest?

2. What essential constituent of the air is found in larger amount in manufacturing districts than in the open country?

3. Can you suggest any reason why the growth of clover in a field improves the soil?

4. When ice is placed in a vessel containing liquid air, the latter boils violently. Explain.

5. Does an electric fan lower the temperature of a room? Why is relief obtained by its use?

6. Would combustion be more intense in liquid than in gaseous air?

7. Taking the volumes of the oxygen and nitrogen in 100 volumes of air as 21 and 78 respectively, calculate the percentages of these elements present by weight.

8. Assuming that dry wood contains 40 per cent carbon, all of which originally came from carbon dioxide in the air, what weight of CO_2 would have to be absorbed by a plant to make 500 g. of wood?

9. What weight of copper would be required to combine with the oxygen in 5 l. of dry air?

10. A tube containing calcium chloride was found to weigh 30.1293 g. A volume of air which weighed 15.2134 g. was passed through the tube, after which the weight of the tube was found to be 30.3405 g. What was the percentage of moisture present in the air?

11. 10 l. of air measured at 20° and 740 mm. passed through limewater caused the precipitation of 0.0102 g. of $CaCO_3$. Find the number of volumes of carbon dioxide in 10,000 volumes of the air.

CHAPTER XIII

SOLUTIONS; THE IONIZATION THEORY

Introduction. In Chapter II a distinction was made between a mixture and a compound. In a typical mixture particles of different properties may be distinguished, so it is not of perfectly uniform character. In a compound every smallest portion is identical in composition with every other portion.

Intermediate between these is a great class of bodies called *solutions*, the most familiar types of which are solutions of solids in liquids. They differ most noticeably from mixtures in that they are of perfectly even character throughout, which fact is usually expressed by saying that they are *homogeneous*. They differ from definite chemical compounds in that their composition can be varied between wide limits. A solution may therefore be defined as a body of homogeneous character whose composition may be varied continuously between certain limits. This definition makes no restrictions as to the physical state of the solution or of its constituents. It includes any combination, such as gases in gases or in liquids, solids in liquids or in solids.

In all solutions we are dealing with two constituents: (1) the medium in which the second body dissolves, which is known as the *solvent*, and (2) the body which dissolves in the solvent, known as the *solute*; thus, in a solution of sugar in water, the water is the solvent and the sugar is the solute. The most familiar types of solutions are those of gases in liquids and solids in liquids.

SOLUTION OF GASES IN LIQUIDS

We have seen that oxygen, hydrogen, and nitrogen are slightly soluble in water. Accurate study has led to the conclusion that all gases are soluble to some extent, not only in water but in many other liquids. The amount of a gas which will dissolve in a liquid depends upon a number of conditions, and these can best be understood by supposing a vessel *B* (Fig. 63) to be filled with the gas and inverted over the liquid *A*. Under these circumstances the gas cannot escape or become mixed with another gas.

Factors affecting the solubility of gases. A number of factors affect the solubility of a gas in a liquid.

1. ***Nature of the gas.*** Other conditions being equal, each gas has its own peculiar solubility, just as it has its own special taste or odor. The solubility of gases varies between wide limits, as will be seen from the following table, which gives the volumes of some well-known gases that will dissolve in 1 l. of water.

SOLUBILITY OF GASES IN ONE LITER OF WATER

NAME OF GAS	VOLUME ABSORBED AT 0° AND UNDER 760 MM. PRESSURE
Ammonia	1298.9 l.
Hydrogen chloride	506.0 l.
Sulfur dioxide	79.79 l.
Hydrogen sulfide	4.37 l.
Carbon dioxide	1.713 l.
Oxygen	0.0496 l.
Nitrogen	0.0233 l.
Hydrogen	0.0214 l.

It will be noted that some gases, such as ammonia, are very soluble. This is due to the fact that the gas in part combines with the water to form a compound.

2. ***Nature of the liquid.*** The character of the liquid has much influence upon the solubility of a gas. Each liquid, such as water, alcohol, or ether, has its own peculiar solvent power. From the solubility of a gas in water no prediction can be made as to its solubility in other liquids.

3. ***Effect of pressure; the law of Henry.*** Increase of pressure always increases the weight of gas going into solution, the increase being proportional to the pressure. This is known as the *law of Henry*, having been formulated by him in 1803. If 1 g. of a gas dissolves in 100 cc. of water at atmospheric pressure, 2 g. will dissolve under 2 atmospheres, provided the temperature remains constant. Under high pressure large quantities of a gas may be dissolved in a liquid. In such solutions, when the pressure is removed, that fraction of the gas escapes that was held in solution by the increased pressure.

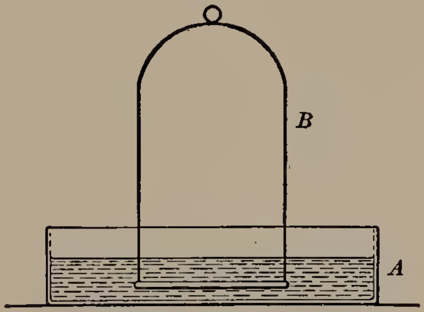


FIG. 63. The solubility of a gas inclosed over water

4. ***Influence of temperature.*** In general, the lower the temperature of the liquid, the larger the quantity of gas which it can dissolve. Thus, 1 l. of water at 0° will dissolve 0.0496 l. of oxygen; at 50°, 0.01837 l.; at 100°, none at all. While most gases can be driven from a liquid by boiling the solution, some cannot. For example, it is not possible to expel hydrogen chloride completely from its solution by boiling.

SOLUTIONS OF SOLIDS IN LIQUIDS

A solid dissolved in a liquid is by far the most familiar type of solution. In the following discussion it should be remembered that we are dealing with true solutions only. Thus, it is sometimes said that zinc dissolves in hydrochloric acid. In this case, however, the solution is preceded by an undoubted chemical reaction whereby the zinc is converted into zinc chloride, and it is this compound which is obtained when the solution is evaporated to dryness. With solutions such as we are now considering, evaporation leaves the solute in its original chemical condition.

Factors affecting the solubility of a solid. The solubility of a solid in a liquid depends upon several factors.

1. *Nature of the solid.* Other conditions being the same, solids vary greatly in their solubility in liquids (see table on opposite page).

No solids are absolutely insoluble, but the amount dissolved may be so small as to be of no significance for most purposes. Thus, barium sulfate, one of the most insoluble of common substances, dissolves in water to the extent of 1 part in 400,000.

2. *Nature of the solvent.* Liquids vary much in their power to dissolve solids. Some are said to be good solvents, since they dissolve a great variety of substances and considerable quantities of them. Others have small solvent power, dissolving few substances, and those to a slight extent only. Broadly speaking, water is the most general solvent, and alcohol is perhaps second in solvent power.

3. *Temperature.* The weight of a solid which a given liquid can dissolve varies with the temperature. Usually it increases rapidly as the temperature rises, so that the boiling liquid dissolves several times the weight which

the cold liquid will dissolve. In some instances, as in the case of sodium chloride (common salt) dissolved in water, the temperature has little influence upon the solubility, and a few solids such as calcium hydroxide (slaked lime) are more soluble in cold water than in hot. The following examples will serve as illustrations:

TABLE OF SOLUBILITY OF SOLIDS

Substance	Formula	Weight dissolved by 100 cc. of water at		
		0°	20°	100°
Calcium chloride .	$CaCl_2$	59.50 g.	74.5 g.	159.0 g.
Sodium chloride .	$NaCl$	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate .	KNO_3	13.30 g.	31.6 g.	246.0 g.
Copper sulfate . .	$CuSO_4$	14.30 g.	21.7 g.	75.4 g.
Calcium sulfate . .	$CaSO_4$	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide .	$Ca(OH)_2$	0.185 g.	0.165 g.	0.077 g.

Molar solutions. In stating the concentration of a solution we may obviously make use of the percentage system. It is often desirable to state the number of formula weights or molecular weights (measured in grams) which a given volume of the solution contains. When as many grams of a substance as there are units in its molecular weight is dissolved so as to make a liter of solution, it is said to be a *molar* or *gram-molecular* solution. Thus, a molar solution of sodium chloride (NaCl) contains 23.00 + 35.46, or 58.46 g., of the solid in 1 l. of the solution.

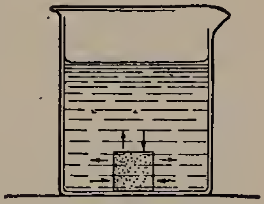


Fig. 64. Diagram illustrating the equilibrium of a saturated solution

Saturated solutions. When a lump of sugar is placed in a small beaker and covered with water, as represented in Fig. 64, it gradually diminishes in size and passes into solution, particles leaving it and diffusing through the solvent. If there is enough sugar, and a long enough time elapses, the concentration of the sugar in the solution reaches a definite limiting value, and we say that the sugar ceases to dissolve and that the solution is *saturated.* There is good reason for thinking that particles continue to leave the lump, but that an equilibrium has been reached, the rate of departure of the particles being equal to the rate of the return of others from the solution. *A saturated solution may therefore be defined as one which is in equilibrium with the undissolved solute.*

FIG. 65. The rapid growth of a crystal suspended in a supersaturated solution

Separation of solids from their solutions. When any given solid separates from its solution, it is usually deposited in crystalline form, each solid having its own definite form. This process is often employed to purify solids, such solvents being selected as will retain the impurities in solution. The separation of a solid from its solution is usually brought about in one of two ways: (1) The solvent may be saturated with the solid at room temperature and the resulting solution set aside. The solvent gradually evaporates and the solid is slowly deposited. (2) Most solids are much more soluble at high temperatures than at low; consequently, if a solution of such a solid is saturated at a high temperature and set aside to cool, then, in most cases (see next paragraph), all of the solid in excess of the quantity required to saturate the solution at the lower temperature crystallizes out.

Supersaturated solutions. When a solution, saturated at a given temperature, is allowed to cool, it sometimes happens that no solid crystallizes out, although the solid may be much less soluble in the cold than in the hot liquid. This is very likely to occur when the solution is rather viscous, like sirup, and is not disturbed in any way. Such a solution is said to be *supersaturated.* That this condition is unstable can be shown by adding a crystal of the solid to the solution. All of the solid in excess of the quantity required to saturate the solution at this temperature will at once crystallize out (Fig. 65). Supersaturation may also be overcome in many cases by vigorously shaking or stirring the solution.

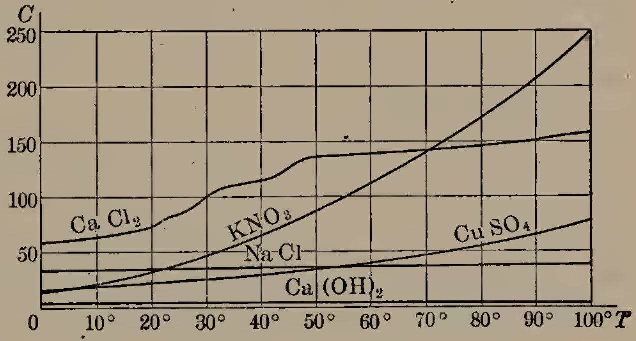


FIG. 66. Some typical solubility curves

Solubility curves. As a rule, the solubility of a solute does not vary with temperature in any regular manner, so we can best represent the facts in a given case by a curve, plotting the temperature as the abscissa (0 T) and the number of grams dissolved in 1 l. as the ordinate (0 C). The diagram (Fig. 66) shows a few typical curves. It will be seen that some substances are very soluble, while others are not. The solubility of some increases rapidly with the increase in temperature, while with others the increase is small.

Characteristic properties of solutions. A few general statements may be made in reference to some characteristic properties of solutions.

1. ***Distribution of the solid in the liquid.*** A solid, when dissolved, tends to distribute itself uniformly through the liquid, so that every part of the solution has the same concentration. The process goes on very slowly unless hastened by stirring or shaking the solution. If a few crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a tall vessel full of water, it will take weeks for the solution to become uniformly colored.

2. ***Boiling point of solutions.*** The boiling point of a liquid is raised by dissolving a solid in the liquid. In general, the extent of this rise is proportional to the molecular concentration of the solution; that is, to the number of gram-molecular weights of the substance dissolved in a definite weight of the solvent. It appears, therefore, that it is not the character of the molecules, but their number alone, which affects the change in the boiling point.

3. ***Freezing point of solutions.*** The freezing point of a liquid is lowered by the presence of a substance dissolved in it. The lowering of the freezing point obeys a law similar to the one which holds for the raising of the boiling point, the extent of the lowering being proportional to the molecular concentration of the solution.

Electrolysis. Pure water does not appreciably conduct the electric current. Moreover, if certain compounds such as sugar are dissolved in the water, the solution is also a nonconductor. If, however, certain other compounds such as sodium chloride or sulfuric acid are dissolved in the water, the resulting solutions are found to be good conductors and are called *electrolytes.* When the current passes through an electrolyte, some chemical change always takes place. This change is called *electrolysis.*

The general method used in the electrolysis of a solution is illustrated in Fig. 67. Two plates or rods (*A* and *B*), made of suitable material, are connected with the wires from a battery (or dynamo) *C* and dipped into the electrolyte, as shown in the figure. These plates or rods are called *electrodes.* The electrode *B* connected with the negative pole of the battery is the negative electrode, or *cathode*, while that connected with the positive pole *A* is the positive electrode, or *anode.*

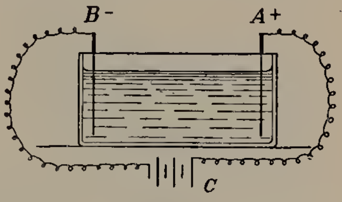


FIG. 67. Diagram showing method of electrolysis of a solution

The theory of ionization. Just why solutions of certain compounds, such as sodium chloride, conduct the electric current, while solutions of other compounds, such as sugar, do not, is not definitely known. It is a significant fact that all those compounds whose solutions are electrolytes affect the boiling points and freezing points of the solvents abnormally; that is, the boiling points and the freezing points are changed more than we should expect. The solids apparently act as though their molecules when dissolved in water broke up into two or more parts, so that the effect is the same as if the number of molecules had been increased. These facts, taken together with the facts discovered in connection with electrolysis, are best explained by a theory first proposed by the Swedish chemist Arrhenius (Fig. 68), and known as the *theory of ionization.* The fundamental ideas in this theory are as follows:

1. ***Formation of ions.*** The molecules of many compounds, when dissolved in water, fall apart, or *dissociate*, into two

or more parts, called *ions*. Thus, sodium nitrate ($NaNO_3$) dissociates into the ions Na and NO_3; sodium chloride (NaCl), into the ions Na and Cl. These ions move about in the solution independently of each other, like independent molecules, and for this reason were given the name *ion*, which means "wanderer."

FIG. 68. Svante August Arrhenius (1859–)

A Swedish chemist, who suggested the theory of ionization

2. ***The electrical charge of ions.*** An ion differs from an atom or molecule in that it carries a large electrical charge. It is evident that the sodium ion must differ in some important way from ordinary sodium, for sodium ions, formed from ordinary salt, give no visible evidence of their presence in water, whereas metallic sodium at once decomposes the water. The electrical charge, therefore, greatly modifies the usual chemical properties of the element.

3. ***The positive charges equal the negative charges.*** The ions formed by the dissociation of any molecule are of two kinds: one is charged with positive electricity and the other with negative. The sum of all the positive charges is always equal to the sum of all the negative charges, and the solution as a whole is therefore electrically neutral. If we represent ionization by the usual chemical equations, with the electrical charges indicated by plus (+) and minus (–) signs following the symbols, the ionization

of the molecules of sodium chloride and sodium sulfate is represented thus:

$$NaCl \longrightarrow Na^+ + Cl^-$$
$$Na_2SO_4 \longrightarrow Na^+, Na^+ + SO_4^{--}$$

Those ions that are positively charged are known as *cations*, while those that are negatively charged are termed *anions*.

4. ***Not all compounds ionize.*** It is assumed that only those compounds ionize whose solutions are electrolytes. Thus, salt ionizes when dissolved in water, for it has been found that the resulting solution is a very good electrolyte. Sugar, on the other hand, does not ionize, for its solution is not a conductor of the electric current.

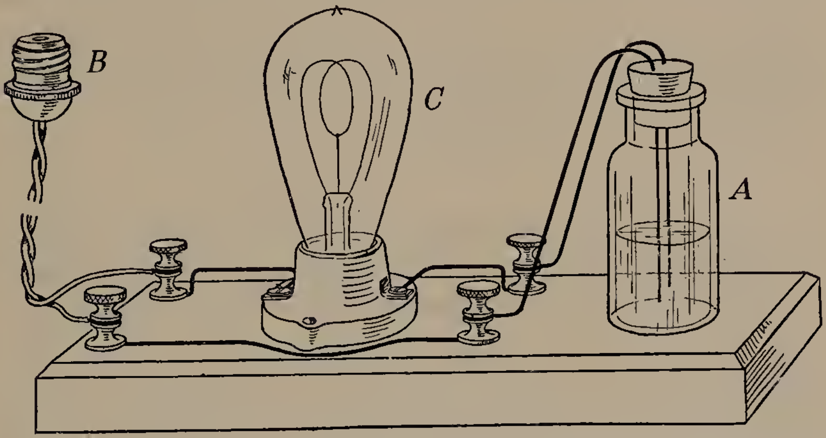


Fig. 69. Apparatus for determining whether or not a solution is an electrical conductor

Fig. 69 illustrates a very convenient apparatus for determining whether a solution is a good conductor. The solution is placed in the bottle *A* and the electrodes are dipped into it. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.

Extent of ionization. Compounds differ greatly among themselves in the ease with which they ionize in solution. Some compounds ionize readily, others only slightly, and others not at all. Again, the extent of ionization varies with the solvent. Thus, the gas known as hydrogen chloride (HCl) is largely ionized when dissolved in water, while in benzene it is not ionized at all. Water is the best ionizing solvent. Moreover, dilution aids ionization. For example, in a concentrated aqueous solution of sodium chloride, only a small percentage of the molecules are ionized, an equilibrium being reached between the molecules decomposing into ions and those forming again from the ions, as expressed in the following equation:

$$NaCl \rightleftarrows Na^+ + Cl^-$$

If the solution is diluted by the addition of more water, the percentage of molecules undergoing ionization increases, and reaches a maximum only in very dilute solutions.

The theory of ionization and the properties of solutions. In order to be of value this theory must be in accord with the chief properties of solutions. Let us now see if the theory is in harmony with certain of these properties.

The theory of ionization and the boiling and freezing points of solutions. We have seen that the boiling point of a liquid is raised in proportion to the number of molecules of a solute dissolved in the liquid. It has been found that *in the case of electrolytes* the boiling point is raised *more* than it should be to conform to this law. If the solute dissociates into ions, the reason for this becomes clear. Each ion has the same effect on the boiling point that a molecule has, and since their number is always greater than that of the molecules from which they were formed, the effect on the boiling point is abnormally great.

In a similar way the theory furnishes an explanation of the abnormal lowering of the freezing point of electrolytes.

The theory of ionization and electrolysis. The changes taking place during electrolysis harmonize very completely with the theory of ionization. This will become clear from a study of the following examples:

1. ***Electrolysis of sodium chloride.*** Fig. 70 represents a vessel in which the electrolyte is a solution of sodium chloride (NaCl). According to the theory of ionization, the molecules of sodium chloride dissociate into the ions Na^+ and Cl^- as soon as the compound dissolves in water. Since the cathode *B* has a large negative charge derived from the battery *C*, the Na^+ ions are attracted to it. On coming in contact with the cathode, they give up their positive charge and are then ordinary sodium atoms. They immediately decompose the water according to the equation

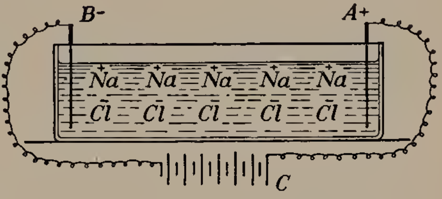


FIG. 70. Diagram illustrating the theory of the electrolysis of sodium chloride (NaCl)

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

In a similar way the chlorine ions (Cl^-) are attracted to the positively charged anode *A*, and upon giving up their charge to it they are set free as chlorine atoms and may either combine with each other to form molecules of chlorine gas, or may attack the water as represented in the equation

$$4\,Cl + 2\,H_2O \longrightarrow 4\,HCl + O_2$$

It is to be carefully noted that the current does not bring about the decomposition of the solute into ions, and that it can pass through the solution only when ions are already present.

2. ***Electrolysis of water.*** The reason for the addition of sulfuric acid to water in the preparation of oxygen and hydrogen by electrolysis (p. 16) can now be made clear. Water itself is not an electrolyte to an appreciable extent, for it does not form enough ions to carry a current. Sulfuric acid (H_2SO_4) dissolved in water is an electrolyte, and dissociates into the ions $2\,H^+$ and SO_4^{--}, each SO_4^{--} ion having two negative charges. In the process of electrolysis of the solution the H^+ ions travel to the cathode, and on being discharged, escape as hydrogen gas. The SO_4^{--} ions, when discharged at the anode, act upon the water, setting free oxygen and once more forming sulfuric acid:

$$2\,SO_4 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + O_2$$

The sulfuric acid can again ionize and the process repeat itself as long as any water is left. Hence the hydrogen and oxygen set free in the electrolysis of water really come *directly* from the acid but *indirectly* from the water.

Properties of electrolytes dependent upon the ions present. When a substance capable of forming ions is dissolved in water, the properties of the solution will depend upon two factors: (1) the ions formed from the substance; (2) the undissociated molecules. Since the ions are usually more active chemically than the molecules, most of the chemical properties of an electrolyte are due to the ions rather than to the molecules.

The solutions of any two substances which give the same ion will have certain properties in common. Thus, all solutions containing the copper ion Cu^{++} are blue, unless the color is modified by the presence of ions or molecules having some other color; aqueous solutions of all chlorides give a precipitate with silver nitrate, since all such solutions contain the chlorine ion Cl^-.

Source of the charges upon the ions. There has been much speculation to account for the electrical charge of the ions. It appears to be very probable that the atoms of the elements are not homogeneous bodies but organized systems, each containing its own number of smaller bodies, which are called *electrons.* These electrons are all alike, and appear to be about $\frac{1}{1800}$ the weight of a hydrogen atom. They can be separated from ordinary matter, so they are capable of existing in the free state. The evidence goes to show that they are really negative electricity, which is therefore a material thing. A body containing more than its normal number of electrons is said to be negatively charged, while one from which some of its normal number of electrons have been removed is said to be positively charged. Electrical energy is the energy of innumerable electrons in very rapid motion.

Applying these views to the electrification of ions, we assume that before union the atoms of sodium and chlorine have each their normal number of electrons. When these combine to form sodium chloride, we have no knowledge as to any disturbance in the distribution of the electrons in the several atoms. When the sodium chloride is dissolved in water, however, it appears that this distribution tends to change. The sodium atom loses one electron and the chlorine atom gains one. The sodium atom is now positively charged, the chlorine negatively; and in this condition they can part from each other to form independent ions. Upon recombination the original condition of the two atoms is restored, and the molecule is electrically neutral. The ions are therefore very different things from the atoms; they should even have different weights, though we cannot verify this experimentally.

EXERCISES

1. Distinguish clearly between the following terms: *electrolysis, electrolyte, ions, solute, solvent, solution, saturated solution,* and *supersaturated solution.*

2. Why does the water from some natural springs effervesce?

3. Why does not the water of the ocean freeze?

4. Why does shaking or stirring make a solid dissolve more rapidly in a liquid?

5. Why will vegetables cook faster when boiled in strong salt water than when boiled in ordinary water?

6. How do you explain the foaming of soda water?

7. Account for the fact that sugar sometimes deposits from sirups, even when no evaporation has taken place.

8. 100 g. of sodium chloride was dissolved in sufficient water to give 1500 cc. of solution. What was the molar concentration?

9. 200 g. of potassium nitrate was dissolved in 120 cc. of boiling water and the solution cooled to 20°. What weight of potassium nitrate separated?

10. A saturated solution of each of the compounds potassium nitrate, sodium chloride, and calcium hydroxide was prepared by heating the solids with 1000 cc. of water. How would the lowering of the temperature affect each solution?

11. 10 g. of common salt was dissolved in water and the solution evaporated to dryness; what weight of solid was left? 10 g. of zinc was dissolved in sulfuric acid and the solution evaporated to dryness; what weight of solid was left?

12. What is the action of sodium upon water? How do you account for the fact that the sodium ions present in a solution of sodium chloride do not decompose the water?

13. The SO_4 ion always bears a double charge of electricity as represented by the expression SO_4^{--}. What action occurs when this ion gives up its charge of electricity, as in the electrolysis of dilute sulfuric acid?

14. What changes should you expect to take place if a current of electricity were passed through an aqueous solution of copper sulfate ($CuSO_4$)? Illustrate by diagram similar to Fig. 70.

15. Contrast the effects in composition produced by adding water to concentrated solutions of sugar and salt respectively.

16. How do you account for the fact that solutions of certain compounds often change in color upon dilution?

CHAPTER XIV

CHLORINE; HYDROGEN CHLORIDE; HYDROCHLORIC ACID

History and occurrence of chlorine. Scheele, who was the first to obtain oxygen in the pure state, was likewise the first to isolate the element chlorine (1774). He obtained the element by the action of hydrochloric acid upon manganese dioxide, a method of preparation which is still used. For years after its discovery chlorine was regarded as a compound of hydrochloric acid with oxygen, but in 1810 the English chemist Davy proved its elementary character.

The most abundant compound of chlorine is sodium chloride, or common salt. This compound is found in sea water and constitutes large solid deposits in various parts of the world (rock salt). Chlorine also occurs in nature in combination with potassium, magnesium, calcium, and, to a limited extent, with some of the other metals.

Preparation. The laboratory method of preparation is different from the commercial method.

1. *Laboratory methods.* Two methods are in common use for the preparation of chlorine in the laboratory. In the first of these hydrochloric acid (that is, an aqueous solution of hydrogen chloride (HCl)) is warmed with manganese dioxide. The latter compound is a black solid and has the formula MnO_2. Manganese tetrachloride ($MnCl_4$), is first formed, but it is unstable and breaks down into manganous chloride ($MnCl_2$) and chlorine (Cl_2), thus:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_4 + 2\,H_2O$$
$$MnCl_4 \longrightarrow MnCl_2 + Cl_2$$

Laboratory apparatus. The manganese dioxide and the hydrochloric acid are brought together in a flask *A* (Fig. 71), and a gentle heat is applied. The chlorine set free passes out through *B*, bubbles through a little water in *C* (which removes any hydrochloric acid carried over with it), and finally through some sulfuric acid in *D*, which dries the gas. Being somewhat soluble in water, it is collected in cylinder *E* by displacement of air, the color showing when the cylinder is full.

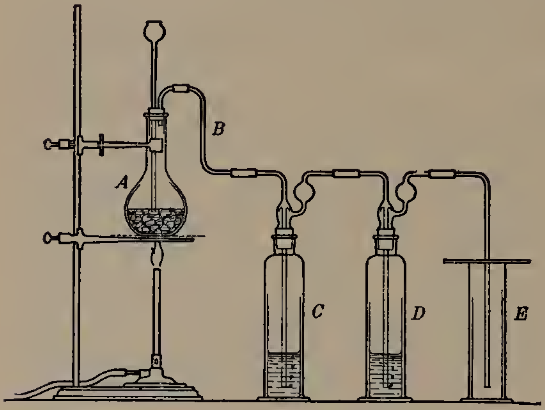


FIG. 71. The preparation of pure chlorine

The second method, often used when a limited supply of chlorine is desired, consists in oxidizing hydrogen chloride according to the equation

$$4\,HCl + O_2 \longrightarrow 2\,H_2O + 2\,Cl_2$$

Free oxygen may be used, but the yield is small. The use of suitable catalytic agents (such as copper sulfate) increases the yield, but it is much more convenient to substitute an oxidizing agent for the free oxygen. The best oxidizing agent for the purpose is the purple-black solid having the formula $KMnO_4$ and known as potassium permanganate. The complete reaction is complex and will be explained more fully in a later chapter; for the present it is only necessary to remember that in a general way the chlorine is liberated according to the above equation, the oxygen being derived from the potassium permanganate. While this method of preparation is somewhat more expensive than the first method, it nevertheless has an advantage in that no heat is required and the rate at which chlorine is formed is easily regulated.

Laboratory apparatus. To obtain chlorine in the laboratory by this method the potassium permanganate is placed in a flask *A* (Fig. 72), and a mixture of equal volumes of concentrated hydrochloric acid and water is added, drop by drop, from a funnel (*B*) provided with a stopcock so that the flow of the liquid can be regulated. (Such a funnel is called a *separatory funnel.*) The reaction takes place at once, and the chlorine evolved through *C* is collected by displacement of air. If a high degree of purity is desired, the gas should be bubbled through sulfuric acid.

2. ***Commercial method.*** It will be recalled that when a solution of sodium chloride is electrolyzed, chlorine is evolved at the anode, while sodium hydroxide (NaOH) is formed at the cathode and remains in solution (p. 155). All of the chlorine prepared for commercial purposes in the United States is obtained in this way. The method has the advantage that sodium chloride is cheap, and that the sodium hydroxide formed in the process has many commercial uses. The chlorine so obtained is either compressed in strong iron cylinders and shipped in this form, or it is passed into slaked lime and forms the solid known as *chloride of lime*, or *bleaching powder* (p. 427), which can be easily shipped and from which the chlorine can be obtained as needed.

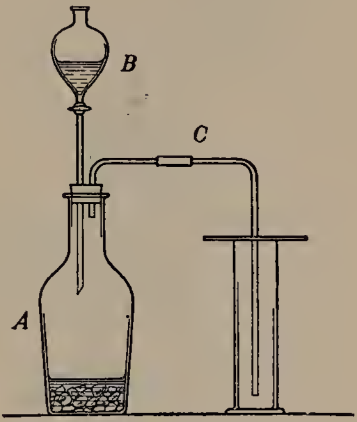


FIG. 72. Preparation of chlorine from potassium permanganate and hydrochloric acid

Properties of chlorine. Chlorine is a greenish-yellow gas which has a peculiar, suffocating odor and produces a very irritating effect upon the throat and lungs. Even when inhaled in small quantities, it often produces all the symptoms of a very hard cold, and in larger quantities may have serious and even fatal effects. Inhaling ether or ammonia gives some relief. Chlorine is nearly 2.5 times as heavy as air, and can therefore be collected by displacement of air. One volume of water under ordinary conditions dissolves about 3 volumes of chlorine.

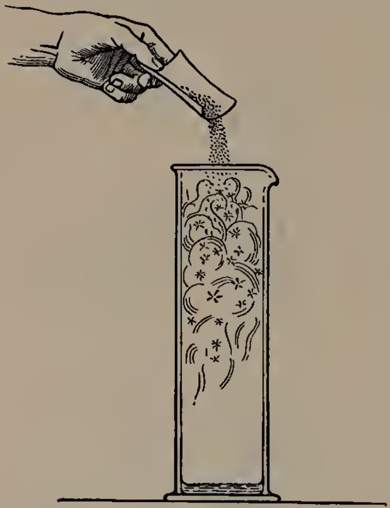


FIG. 73. The burning of powdered metals in chlorine gas

Chemical conduct of chlorine. At ordinary temperatures chlorine is one of the most active of all elements. Its activity may be described under a number of distinct headings.

1. *Action on elements other than hydrogen.* Many of the elements combine directly with chlorine even at ordinary temperatures. Thus, phosphorus burns in a current of the gas, while antimony and arsenic, in the form of a fine powder, at once burst into flame when dropped into jars of the gas (Fig. 73). When a strip of copper foil heated to redness is dropped into chlorine, the two elements unite with incandescence. Even inactive metals like gold and platinum are tarnished by the gas. The compounds formed by the union of chlorine with another element are called *chlorides*, and constitute a very important group. Common salt, for example, is chloride of sodium (NaCl).

2. ***Action on hydrogen.*** Chlorine has a strong affinity for hydrogen, uniting with it to form gaseous hydrogen chloride (HCl). A jet of hydrogen burning in the air continues to burn when introduced into a jar of chlorine, giving a somewhat luminous flame (Fig. 74). A mixture of the two gases explodes violently when a spark is passed through it or when it is exposed to bright sunlight. In the latter case it is the light and not the heat which starts the action.

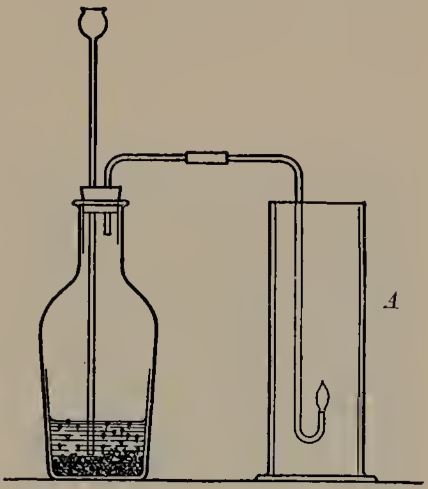


FIG. 74. The burning of a jet of hydrogen in an atmosphere of chlorine

3. ***Action on compounds of hydrogen.*** Not only will chlorine combine directly with free hydrogen, but it will often abstract the element from its compounds. Thus, when chlorine is passed into a solution of hydrogen sulfide, the chlorine combines with the hydrogen, while sulfur is set free in accordance with the following equation:

$$Cl_2 + H_2S \longrightarrow 2\,HCl + S$$

The same tendency is very strikingly seen in the action of chlorine upon turpentine. The latter substance is largely made up of compounds which have the composition represented by the formula $C_{10}H_{16}$. When a strip of paper moistened with warm turpentine is placed in a jar of chlorine, the hydrogen of the turpentine combines with the chlorine to form hydrogen chloride, and the carbon is set free in the form of a black solid.

4. ***Action upon water.*** The reaction between chlorine and water is of great importance, since the use of chlorine as a bleaching agent is based primarily upon it. When the chlorine is passed into water both hydrochloric acid and hypochlorous acid (HClO) are formed:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

The hypochlorous acid, however, is a very unstable compound and breaks down slowly in the dark but rapidly in the sunlight, as follows:

$$2\,HClO \longrightarrow 2\,HCl + O_2$$

The effect of sunlight in increasing the action of chlorine upon water may be shown in the following way: If a long tube of rather large diameter is filled with a saturated solution of chlorine in water and inverted in a vessel of the same solution (as shown in Fig. 75), and the apparatus is placed in bright sunlight, bubbles of gas will soon be seen to rise through the solution and collect in the tube. An examination of this gas will show that it is oxygen.

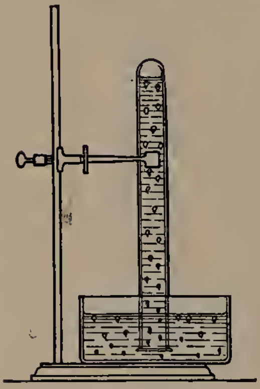


FIG. 75. Decomposition of water by chlorine in the sunlight

The decomposition of water through the action of chlorine is also greatly increased in the presence of some substance which combines with the oxygen as fast as it is set free. Consequently a solution of chlorine in water is a good oxidizing agent, and, indeed, it is often used as such.

5. ***Action upon color substances; bleaching action.*** Chlorine possesses a powerful bleaching action. Strips of highly colored cloth, when moistened with water and placed in jars of chlorine, rapidly lose their color. The presence of water is essential to the change, as may be shown by

placing strips of the dry cloth in chlorine from which the moisture has been removed by bubbling it through sulfuric acid. Under these conditions the color of the cloth remains unchanged. It is probable that the bleaching action of chlorine consists first in its reaction with water to form hypochlorous acid (p. 164). This acid then decomposes, the resulting oxygen reacting with the color substance of the cloth to form colorless compounds. It is evident, therefore, that chlorine will bleach only those materials the coloring matters of which are changed by its action into colorless compounds. It has no bleaching action on such color substances as carbon, and hence does not affect printer's ink made from carbon. It cannot be used for bleaching certain substances like silk and straw, since it injures the fabric.

Fig. 76. Bleaching colored cloths by moist chlorine

Certain foods, such as dried fruits and the lower grades of flour, are also bleached. The bleaching of flour was formerly prohibited, but is now largely practiced, since it enables the miller to obtain a larger yield of white flour.

Fig. 76 illustrates the bleaching action of chlorine. Strips from the same piece of cloth are suspended in three jars, of which the first contains air, the second *dry* chlorine, and the third *moist* chlorine. It will be noted that the dry chlorine has almost no bleaching action, while the moist chlorine has partly removed the color.

6. *Action as a germicide.* Chlorine has marked germicidal properties, and the free element, as well as the compounds from which it is easily liberated, are used as disinfectants.

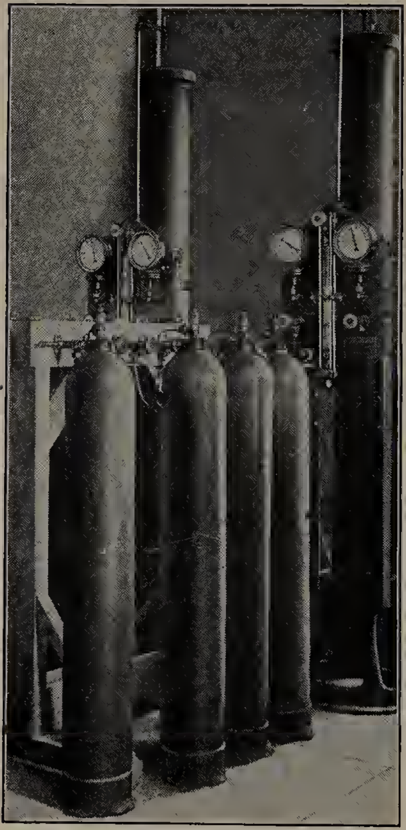


FIG. 77. Chlorine stored in bombs, for use in water purification

Uses of chlorine. As has been stated above, chlorine is an excellent germicide and bleaching agent, and large quantities of the element are used for these purposes. The various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored by the presence of natural coloring matter. Hence, if a white fabric is desired, bleaching is necessary. This was formerly accomplished by exposing the fabric to the action of the air and sunlight, but many days were required for the completion of the process. The same results are now obtained in a very short time by the use of chlorine.

As a rule chlorine is used commercially in the form of bleaching powder. The chlorine present in this substance can be liberated easily and utilized as desired. Increasing amounts of the free element are being used in manufacturing processes and as an agent for destroying the microörganisms in city water supplies (Fig. 77). Many of the gas bombs used in the great war contained chlorine.

Nascent state. It will be noticed that when oxygen is set free from water by chlorine, it is at that instant able to do what ordinary oxygen gas cannot do, for it bleaches substances which would remain unchanged in dry air or pure oxygen. It is generally true that the activity of an element is greatest at the instant of its liberation from its compounds. To express this fact, elements at the instant of liberation are said to be in the *nascent state*, the word *nascent* being derived from a Latin word meaning "to be born." This greater activity is usually accounted for by supposing that an element at the instant of liberation from a compound is in the form of atoms, and is therefore more reactive than after the atoms have combined to form molecules.

Hydrogen chloride (HCl). We have seen that hydrogen and chlorine combine directly (Fig. 74) to form the gaseous compound known as hydrogen chloride. In the laboratory it is more convenient to prepare this compound in a different way, as described in the following paragraph.

Laboratory preparation. Hydrogen chloride is ordinarily prepared in the laboratory by the action of sulfuric acid upon sodium chloride. Sodium sulfate (Na_2SO_4) and hydrogen chloride are formed according to the following equation:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

It will be noted that in this reaction the sodium of the sodium chloride exchanges places with the hydrogen of the sulfuric acid. Such a reaction is called a *double decomposition.*

To prepare the gas, the dry sodium chloride is placed in a flask *A* (Fig. 78), sulfuric acid is added, and the flask gently warmed. The hydrogen chloride is rapidly given off and can be collected by displacement of air. To prepare a solution of the gas the end of the delivery tube is fixed *just above* the level of some water in the cylinder *B*. The gas is very soluble and is absorbed as fast as it escapes from the tube. The sodium sulfate formed is a white solid and remains in the flask *A*.

Commercial preparation. The laboratory method is likewise used in the preparation of hydrogen chloride on a commercial scale. The compound is also prepared commercially by heating sodium chloride with the white solid compound known as sodium hydrogen sulfate ($NaHSO_4$) (p. 207):

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

In either case the hydrogen chloride liberated is passed into water, in which it readily dissolves, the solution constituting the *hydrochloric acid* of commerce. When the materials are pure a colorless solution is obtained. The most concentrated solution has a density of about 1.2 and contains approximately 43 per cent of hydrogen chloride. The ordinary, or commercial, hydrochloric acid sold on the market is usually colored yellow by impurities. This impure acid is often called *muriatic acid*.

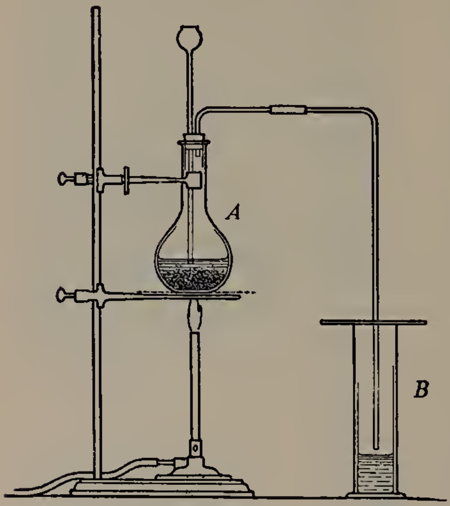


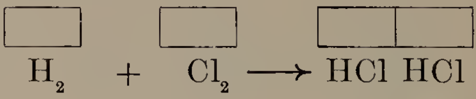
FIG. 78. The preparation of a solution of hydrogen chloride

Properties of hydrogen chloride. Hydrogen chloride, a colorless gas, is 1.26 times as heavy as air. When inhaled, it has an irritating and suffocating effect. At 0° it is condensed to the liquid state by a pressure of 28 atmospheres. The resulting liquid is colorless, boils at – 82.9°, and solidifies at – 113°. This liquid does not conduct electricity, has no action upon metals, and in general is very inactive. Hydrogen chloride is very soluble in water, 1 volume of the latter under standard conditions dissolving 506 volumes of the gas. The density of its aqueous solutions increases with the amount of gas dissolved, as shown in the following table, which gives the percentage by weight of hydrogen chloride present in solutions of various densities, the measurements being taken at 15°.

PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY
5.69	1.0284	20.04	1.1006	35.02	1.1779
10.17	1.0507	25.06	1.1265	40.09	1.2013
15.22	1.0761	30.00	1.1526	43.40	1.2134

The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask *A* (Fig. 79) is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask *B*, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask *A* is drawn out to a rather fine jet. By blowing into the tube *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from *B* into *A*, until virtually all the hydrogen chloride is absorbed. It is evident that the connection must be air-tight.

Composition of hydrogen chloride. The composition of hydrogen chloride can be determined by the electrolysis of its aqueous solution. When hydrogen chloride is electrolyzed, the hydrogen of the compound is evolved at the cathode and the chlorine at the anode. A special form of apparatus is required, in order to avoid the difficulties arising from the marked solubility of the chlorine in water. When the experiment is carried out, it is found that the volume of the hydrogen liberated is exactly equal to that of the chlorine. Conversely, it is possible to show by experiment that when hydrogen and chlorine combine, they always do so in the ratio of 1 volume of hydrogen to 1 volume of chlorine; moreover, the product is always 2 volumes of hydrogen chloride. These relations may be shown graphically in the following way:



$$H_2 + Cl_2 \longrightarrow HCl\ HCl$$

Since chlorine is 35.18 times as heavy as hydrogen, it follows that 1 part by weight of hydrogen combines with 35.18 parts by weight of chlorine to form 36.18 parts by weight of hydrogen chloride.

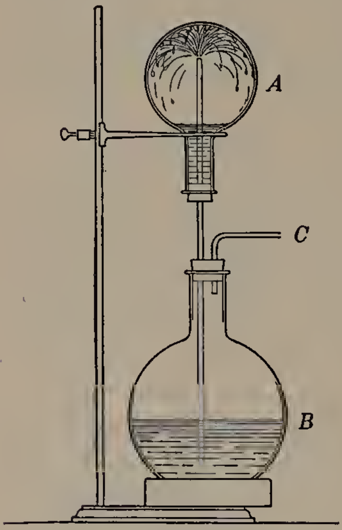


Fig. 79. Apparatus to show the extreme solubility of hydrogen chloride in water

Hydrochloric acid. Hydrogen chloride itself, as well as its solution in nonionizing solvents, has but little chemical activity. On the other hand, its solution in water, namely *hydrochloric acid*, has marked chemical properties and constitutes one of the most important members of that general class of compounds known as acids (p. 179). It has a sour taste and changes the colors of certain organic compounds. Thus, blue litmus (a colored compound obtained from certain lichens) is turned red when a little hydrochloric acid is added to it.

Hydrochloric acid acts upon many of the metals, such as iron, zinc, and sodium, liberating the hydrogen and forming chlorides of the metals:

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$$
$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$2\,Na + 2\,HCl \longrightarrow 2\,NaCl + H_2$$

It also acts upon the hydroxides of the metals, such as sodium hydroxide ($NaOH$), as shown in the following equation:

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

EXERCISES

1. Consult the dictionary for the meaning of the word *chlorine*.

2. Why must chlorine water be kept in the dark?

3. Calculate the weight of 10 l. of chlorine. What weight of the compound HCl would be required for the preparation of 10 l. of chlorine?

4. Why not collect chlorine over water as hydrogen and oxygen were collected?

5. What volume of chlorine can be prepared from 100 kg. of sodium chloride?

6. 10 l. of chlorine will combine with how many liters of hydrogen? How many liters of hydrogen chloride will be formed?

7. Distinguish definitely between hydrogen chloride and hydrochloric acid.

8. What weight of common salt is necessary for the preparation of 100 l. of hydrogen chloride?

9. In the preparation of hydrogen chloride (Fig. 78) why not have the exit tube dip below the surface of the water in *B*?

10. (*a*) What is the density of hydrochloric acid containing 30 per cent of hydrogen chloride? (See table, p. 169.) (*b*) What would 1 l. of this acid weigh? (*c*) What weight of hydrogen chloride would it contain? (*d*) What weight of sodium chloride would be necessary to prepare this weight of hydrogen chloride?

CHAPTER XV

SODIUM; SODIUM HYDROXIDE

Metals and nonmetals. The chemist finds it convenient to divide the elements into two general groups known as the *metals* and the *nonmetals.* It is the chemical conduct of an element that determines to which of these two groups it belongs. This distinction will be discussed in a later chapter. For the present it is only necessary for us to remember that all the metals are solids, except mercury, which is a liquid; that as a rule they are good conductors of heat and electricity and, with the exception of gold and copper, they have a silvery luster. Most of the metals have a high density; a few, such as aluminium and magnesium, however, are comparatively light, while three, namely lithium, sodium, and potassium, are so light that they will float on water.

The elements so far studied, namely oxygen, hydrogen, nitrogen, the rare elements in the atmosphere, and chlorine, are all nonmetals. Having studied a number of nonmetals it is advisable now to study some metal, and the one known as sodium best serves our purposes.

History of sodium. The isolation of sodium dates back to the year 1807. At that time the compounds now known as sodium hydroxide and potassium hydroxide were well known, but they were regarded as elementary in character. In 1807 Sir Humphry Davy (Fig. 80), while studying the effect of the electric current upon various substances, succeeded in decomposing these compounds and from them obtained both sodium and potassium.

Occurrence of sodium. Because of its great activity, sodium does not occur in nature in a free state. The most familiar compound of the element found in nature is sodium chloride. This is a constituent of all sea waters and mineral waters and forms large solid deposits in various parts of the world. The element also occurs as a constituent of many rocks, and its compounds are therefore present in the soil formed by their disintegration. Other compounds of sodium often found in nature are sodium nitrate (known commercially as Chile saltpeter), sodium carbonate, and sodium borate, or borax.

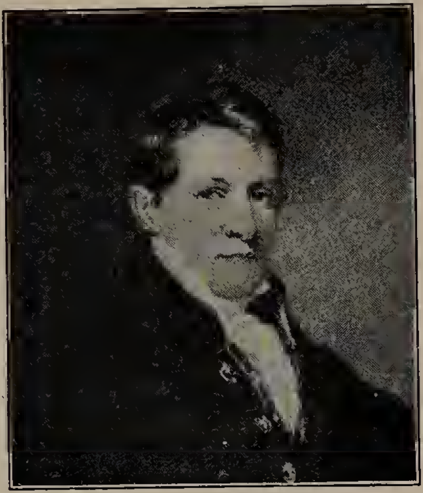


FIG. 80. Sir Humphry Davy (1778–1829)

A distinguished English scientist who invented the safety lamp, demonstrated the nature of chlorine, and first isolated the elements sodium and potassium

Preparation of sodium. For many years the most economical method known for preparing sodium consisted in heating sodium carbonate (a white solid having the formula Na_2CO_3) with carbon:

$$Na_2CO_3 + 2\,C \longrightarrow 2\,Na + 3\,CO$$

At present it is prepared by the electrolysis of its hydroxide, a white solid compound having the formula NaOH. It is necessary to carry on the process in the absence of water, because the metal acts upon water with great vigor (p. 39). Since it is impossible to obtain the element by the electrolysis of a solution of the hydroxide, the solid compound is heated until it melts, and the current of electricity is then passed through the resulting liquid. Sodium is prepared at Niagara Falls, where water power is utilized for generating the electric current. The process is a difficult one to carry out, so that sodium is not a cheap metal.

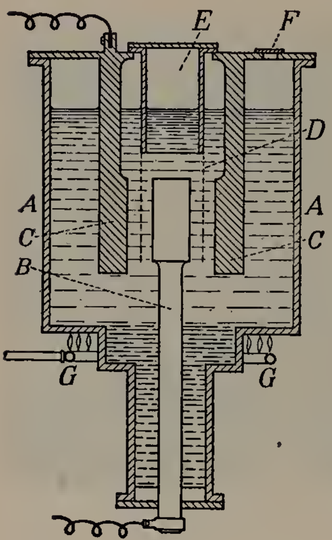


FIG. 81. A Castner cell for the electrolytic production of metallic sodium

Commercial preparation (Castner's process). At Niagara Falls sodium is prepared by the electrolysis of fused sodium hydroxide by a process devised by Castner. The apparatus consists of a cylindrical iron vessel *A*, *A* (Fig. 81), through the bottom of which extends an iron rod *B*, which serves as the cathode. The iron anodes *C*, *C*, several in number, are suspended around the cathode, but are kept from touching it by a cylinder of iron gauze *D*, which is fastened to the vessel *E*. The lower part of the vessel *A*, *A* is filled with molten sodium hydroxide, which, on cooling, holds the cathode in position. The heat generated by the current is ordinarily sufficient to keep the hydroxide in the upper portion of the vessel fused; however, the apparatus is supplied with a row of gas burners *G*, *G*, which may be utilized if additional heat is required. Sodium and hydrogen are liberated at the cathode and, rising to the surface, collect in vessel *E*. The hydrogen escapes by lifting the cover of the vessel, while the sodium, protected from the air by the hydrogen, is skimmed or drawn off from time to time. Oxygen is liberated at the anodes and escapes through the opening *F* without coming in contact with either the sodium or the hydrogen. Sodium has also been prepared by the electrolysis of fused sodium chloride.

Properties and uses. Sodium is a soft, silver-white metal, slightly lighter than water. It melts at 97.5° and boils at 877°. It is very active chemically, combining readily with most of the nonmetallic elements such as oxygen and chlorine. It liberates hydrogen from the common acids (p. 179) and decomposes water, forming sodium hydroxide and hydrogen (p. 39):

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

When exposed to the air, sodium rapidly tarnishes, owing to its combination with oxygen and carbon dioxide. On this account it is often kept immersed in kerosene, since it has no action upon this liquid.

Compounds of sodium. Sodium forms many useful compounds. One of these, sodium hydroxide, is a typical member of that important class of compounds known as *bases*, and it is desirable for us to study its properties at this time; the discussion of the other compounds of sodium may well be deferred to a later chapter.

Sodium hydroxide (caustic soda) (NaOH). This compound is a white solid and, as we have seen, may be prepared by the action of sodium upon water. It is only necessary to bring the sodium and water in contact with each other. The resulting sodium hydroxide dissolves in the water as fast as it is formed, and may be recovered by the evaporation of the water. Since sodium is a comparatively expensive metal, it is evident that this method is not an economical one. Two general processes are now used for preparing the compound on a commercial scale.

1. *Action of calcium hydroxide upon sodium carbonate.* This process consists in treating calcium hydroxide (slaked lime) suspended in water with sodium carbonate:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,NaOH$$

The calcium carbonate ($CaCO_3$) is precipitated as a white, insoluble solid, leaving the sodium hydroxide in solution.

While this is an old process it still remains the chief one for the production of the hydroxide. Manufacturers of sodium carbonate often utilize a portion of their product in the preparation of the hydroxide, so that the manufacture of these two compounds is often carried out in the same plant.

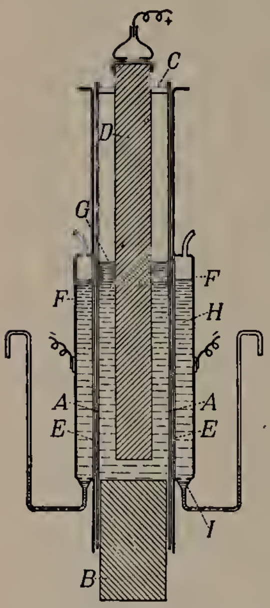


Fig. 82. A Townsend cell for the production of sodium hydroxide

2. *Electrolytic methods.* By the newer method sodium hydroxide is obtained by the electrolysis of sodium chloride. The products of the electrolysis are sodium hydroxide, hydrogen, and chlorine (p. 155). The chief difficulty in this process is to prevent the chlorine and the hydroxide from acting upon each other. This is usually done by separating, by means of a porous partition, the anode and cathode compartments of the cell in which the electrolysis is effected. A number of different cells have been devised for carrying out the process; at present one of the most successful of these is that devised by Townsend and known by his name.

Commercial preparation by the Townsend cell. A section of this cell is shown in Fig. 82. The anode compartment is formed by the partition, or diaphragm, *A*, *A*, a nonconducting bottom *B*, and a lid *C*. The diaphragm is made of asbestos cloth painted over with a mixture of iron oxide and asbestos fiber. Through the lid *C* extends the graphite anode *D*. The diaphragm is set firmly against the perforated iron cathode plate *E*, *E*, which is in turn held in place by the iron sides *F*, *F*, the space between the plate and the iron sides forming the cathode compartment. The anode compartment is partly filled with saturated salt solution *G*, and the cathode compartment with kerosene *H*. Since the level of the salt solution is above that of the kerosene, the solution slowly penetrates the diaphragm, and some of the salt, coming in contact with the cathode, is changed into the hydroxide. The resulting solution of the chloride and hydroxide enters the anode compartment and, being heavier than the kerosene, sinks to the bottom and is drawn off through the side tubes *I*. The chloride, being much less soluble than the hydroxide, is separated by partial evaporation of the solution. The hydrogen and the chlorine that are set free are led off through tubes, and the chlorine is used in the preparation of bleaching powder.

Properties of sodium hydroxide. Sodium hydroxide is a brittle white crystalline substance which rapidly absorbs water and carbon dioxide from the air. As the name *caustic soda* indicates, it is a very corrosive substance, having a disintegrating action on most animal and vegetable tissues. It is very soluble in water, and the resulting solution is soapy to the touch and has a bitter taste. The solution turns red litmus blue, reversing the color change produced on litmus by hydrochloric acid. Its reaction with hydrochloric acid has been described (p. 171). It is used in a great many chemical industries, its chief use being in the manufacture of soap. As a household article it is sold under the name of *lye*.

EXERCISES

1. What is the word from which the symbol of sodium is derived? (Consult dictionary.)

2. Is sodium one of the abundant elements? (Consult Clarke's table, p. 19.)

3. What is the approximate weight of the sodium in your body?

4. What weight of sodium hydroxide is necessary for the preparation of 1 kg. of sodium?

5. When sodium acts upon water, what volume of hydrogen is liberated for each gram of sodium consumed?

6. How many pounds of sodium chloride are necessary for the preparation of 1 ton of caustic soda?

7. Calculate the percentage composition of sodium hydroxide.

8. Write the equation for the reaction between sodium hydroxide and hydrochloric acid.

9. What weight of sodium hydroxide can be obtained from 500 g. of sodium carbonate?

10. How could you tell whether a given solution contains sodium hydroxide or hydrochloric acid, if you knew that one of these is present?

CHAPTER XVI

ACIDS, BASES, AND SALTS; NEUTRALIZATION

Introduction. The great majority of the compounds to be described in the course of our study belong to one of three classes, known as *acids*, *bases*, and *salts*. We have already studied the properties of hydrochloric acid, as well as those of the well-known base, sodium hydroxide. Moreover, sodium chloride, formed by the action of hydrochloric acid upon sodium hydroxide, is a typical salt. Having learned some facts about a representative of each of these classes, we shall now proceed to a more careful study of the characteristics of each class.

The common acids. It will be recalled that hydrochloric acid consists of a solution of hydrogen chloride in water. All of the other common acids used so largely in the industries and in chemical laboratories are aqueous solutions of definite compounds. Thus, nitric acid is a solution of the liquid known as hydrogen nitrate, the formula of which is HNO_3; sulfuric acid is a solution of the thick oily liquid called hydrogen sulfate, whose formula is H_2SO_4. For most purposes it is not necessary to make a distinction between the name of the compound and its solution in water, and both are frequently called acids.

Characteristics of acids. A study of the acids reveals the fact that, while the individual members of the class may differ from each other in many of their properties, they all possess certain fundamental characteristics. These characteristics are as follows: (1) All compounds forming acids in solution contain hydrogen. (2) They react with the hydroxides of metals, in which reaction the hydrogen of the acid combines with the hydroxyl group (OH) of the base to form water. Thus, hydrochloric acid and sulfuric acid react with sodium hydroxide as indicated in the following equations:

$$HCl + NaOH \longrightarrow NaCl + H_2O \text{ (or HOH)}$$
$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$$

(3) As a general rule, acids act upon certain metals, dissolving the metals. In this reaction the metal displaces the hydrogen of the acid. Thus, zinc reacts with hydrochloric acid and sulfuric acid as shown in the following equations:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

(4) The solutions have a sour taste and change the color of certain compounds known as *indicators*. Thus, blue litmus turns red on the addition of an acid. (5) The solutions are electrolytes, and when a current of electricity is passed through them, hydrogen is evolved at the cathode.

The compounds forming acids ionize when dissolved in water; thus,

$$HCl \longrightarrow H^+, Cl^-$$
$$HNO_3 \longrightarrow H^+, NO_3^-$$
$$H_2SO_4 \longrightarrow H^+, H^+, SO_4^{--}$$

It will be noted that the one constituent common to all acids is the hydrogen ion, H^+. Accordingly, the properties which all of these acids have in common, such as their action on metals and their hydroxides, must be due to the hydrogen ions. From the standpoint of the ionization theory, therefore, we may define an acid as a solution containing hydrogen ions.

Undissociated acids. When compounds whose aqueous solutions form acids are perfectly free from water, they have no real acid properties. Neither do they have acid properties when they are dissolved in liquids, like benzene, which do not have the power of dissociating them into ions. For example, a benzene solution of hydrogen chloride has no action on litmus; neither does it dissolve metals.

The common bases. In addition to sodium hydroxide, the common bases include potassium hydroxide (KOH) and calcium hydroxide, $Ca(OH)_2$. These are white solids soluble in water. The very soluble bases with most pronounced basic properties are often called *alkalies.* While these compounds are often called bases, yet pronounced basic properties are exhibited only by their solutions in water.

Characteristics of bases. The class characteristics of the bases are as follows: (1) The compounds contain hydrogen, oxygen, and a metal. (2) They react with acids, the hydroxyl group (OH) of the base combining with the hydrogen of the acid. (3) Their solutions reverse the color change produced in indicators by acids; thus, they turn red litmus blue. (4) Their solutions are conductors of electricity, and when these solutions are electrolyzed the metal is set free at the cathode.

When dissolved in water, the molecules of the base dissociate into two kinds of ions. One of these is always composed of the group (OH), and is the anion. It is called the *hydroxyl* ion. The remainder of the molecule, which usually consists of a single atom, is the cation; thus,

$$NaOH \longrightarrow Na^+, OH^-$$

Since all bases produce hydroxyl anions, while the cations of each are different, the properties which all bases have in common when in solution must be due to the hydroxyl ions. From the standpoint of the ionization theory, therefore, we may define a base as a solution containing hydroxyl ions.

Neutralization. When an acid and a base are brought together in solution in the proper proportion, the characteristic properties of each disappear. It is evident, therefore, that the acid and base must have reacted with each other to form one or more new compounds which are neither acid nor basic in character. What really happens is that the hydrogen of the acid and the hydroxyl group (OH) of the base combine to form water, while the remaining constituents of the acid and base unite to form a compound which belongs to the class of compounds known as salts. These facts are shown by the following typical equations:

$$HCl + NaOH \longrightarrow NaCl + H_2O \text{ (or HOH)}$$
$$HNO_3 + KOH \longrightarrow KNO_3 + H_2O$$
$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\,H_2O$$

In all such reactions the acid and base are said to neutralize each other, and the process is termed *neutralization.*

Since the reactions expressed in the above equations take place only in the presence of water, it is evident that from the standpoint of the ionization theory we are really dealing here with ions rather than with compounds. Now, experiments show that hydrogen ions (H^+) and hydroxyl ions (OH^-) cannot exist together in solution to any appreciable extent, but at once combine to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

Considered from this standpoint, neutralization consists in the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water. To express this fact the above reactions should be written as follows:

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$
$$K^+, OH^- + H^+, NO_3^- \longrightarrow K^+, NO_3^- + H_2O$$
$$Ca^{++}, (OH^-)_2 + (H^+)_2, SO_4^{--} \longrightarrow Ca^{++}, SO_4^{--} + 2\,H_2O$$

It will be observed that in neutralization the cation of the base and the anion of the acid are not changed, but remain as ions in the solution. If now the water present is expelled by evaporation, the two ions unite to form a compound which, with few exceptions, is a solid and remains as a residue in the dish. Thus, the ions Na^+ and Cl^- unite to form the white solid NaCl; similarly, the ions K^+ and NO_3^- unite to form potassium nitrate (KNO_3), while the ions Ca^{++} and SO_4^{--} unite to form calcium sulfate ($CaSO_4$).

Neutralization a definite act. If two solutions, one of a base and the other of an acid, are prepared, experiment has shown that a given volume of the acid will invariably require a perfectly definite volume of the base for its neutralization.

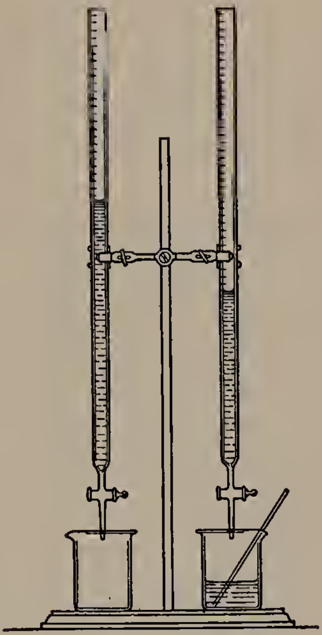


FIG. 83. Two burettes used in proving that neutralization is a definite act

The experiment is most easily performed with the aid of burettes (Fig. 83), which are graduated tubes furnished with a stopcock at one end. The one is filled to the zero mark with the acid solution, the other with the basic. A measured volume of the one solution is drawn off into a small beaker, a few drops of an appropriate indicator added, and the second solution run in with constant stirring until the indicator just turns color. If the concentration of each solution is accurately known, it is easy to calculate, from the volumes required for neutralization, the ratio by weight between the acid and the base taking part in the action. Experiment shows that this ratio always bears a simple relation to that between the molecular weights of the reacting substances. Such a reaction as is indicated in the equation

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$

is therefore perfectly definite, and if we know the weight of an acid employed, we can calculate the weight of the base required to neutralize the acid and also the weight of the salt formed.

Heat of neutralization. If neutralization is due to the union of hydrogen ions with hydroxyl ions, and nothing more, it follows that when a given weight of water is formed in neutralization, the heat set free should always be the same, no matter from what acid and base the two kinds of ions have been supplied. Careful experiments have shown that this is the case, provided no other reactions take place at the same time. When one gram-molecule (18 g.) of water is formed in neutralization, 13,790 cal. of heat are set free. This is represented in the equations

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O + 13{,}790 \text{ cal.}$$
$$K^+, OH^- + H^+, NO_3^- \longrightarrow K^+, NO_3^- + H_2O + 13{,}790 \text{ cal.}$$
$$Ca^{++}, (OH^-)_2 + (H^+)_2, SO_4^{--} \longrightarrow Ca^{++}, SO_4^{--} + 2\,H_2O + 2 \times 13{,}790 \text{ cal.}$$

Salts. We have seen in the process of neutralization (1) that the cation of the base and the anion of the acid are not changed, but remain as ions in the solution; (2) that if the water present is expelled by evaporation, the two ions unite to form a compound. The compounds formed in this way by the union of the cation of the base and the anion of the acid are termed *salts.*

The following equations represent the reactions taking place in the formation of some typical salts.

$$\begin{aligned} HCl + NaOH &\longrightarrow NaCl + H_2O \\ HCl + KOH &\longrightarrow KCl + H_2O \\ 2\,HCl + Ca(OH)_2 &\longrightarrow CaCl_2 + 2\,H_2O \\ HNO_3 + KOH &\longrightarrow KNO_3 + H_2O \\ H_2SO_4 + Zn(OH)_2 &\longrightarrow ZnSO_4 + 2\,H_2O \end{aligned}$$

Relation of salts to acids. The compounds represented by the formulas NaCl, KCl, $CaCl_2$, KNO_3, $ZnSO_4$ are all salts. If we examine the formulas of these salts carefully, we shall see that the compounds represented by these formulas differ from the acids from which they are prepared in that an atom of a metal has been substituted for one or more of the hydrogen atoms of the acid. From this standpoint, *a salt may be regarded as a compound which may be derived from an acid by displacing the hydrogen of the acid by a metal.* It is customary to speak of the salts derived from a certain acid as salts of that acid. Thus, NaCl, KCl, and $CaCl_2$ are all salts of hydrochloric acid. Similarly, KNO_3 is a salt of nitric acid, while $ZnSO_4$ is a salt of sulfuric acid.

Salts are also formed when a metal dissolves in an acid, as illustrated in the following equations:

$$\begin{aligned} Zn + 2\,HCl &\longrightarrow ZnCl_2 + H_2 \\ Fe + H_2SO_4 &\longrightarrow FeSO_4 + H_2 \end{aligned}$$

In general, we might expect each acid to form as many salts as there are metals, and in most cases this is the fact.

Ionization of salts. All salts that dissolve in water ionize in solution, the metal of the salt forming the cation, while the rest of the molecule forms the anion, as shown in the following equations:

$$\begin{aligned} NaCl &\longrightarrow Na^+, Cl^- \\ ZnSO_4 &\longrightarrow Zn^{++}, SO_4^{--} \\ KNO_3 &\longrightarrow K^+, NO_3^- \end{aligned}$$

It will be seen that salts differ from acids and bases in that the solutions have no common ion. It follows that salts do not have so many common characteristics as do acids and bases.

Normal salts; acid salts. It is evident that sodium hydroxide can act upon hydrochloric acid in but one proportion:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

With sulfuric acid, however, the reaction may take place according to either of the following equations, depending upon the relative weights of sodium hydroxide used:

$$\begin{aligned} NaOH + H_2SO_4 &\longrightarrow NaHSO_4 + H_2O \\ 2\,NaOH + H_2SO_4 &\longrightarrow Na_2SO_4 + 2\,H_2O \end{aligned}$$

It will be observed that in the one salt ($NaHSO_4$) only a portion of the hydrogen of the sulfuric acid has been displaced by the metal, while in the other (Na_2SO_4) all of the hydrogen has been displaced. To distinguish between these two classes of salts, the former is said to be an *acid salt*, while the latter is termed a *normal salt.*

Acid salts when dissolved in water give hydrogen ions in addition to the ions characteristic of salts; thus,

$$NaHSO_4 \longrightarrow Na^+, H^+, SO_4$$

They have, therefore, the properties of an acid as well as those of a salt.

Basic salts. When an acid such as hydrochloric acid acts upon a base such as calcium hydroxide, the reaction may take place in either of the following ways:

$$HCl + Ca(OH)_2 \longrightarrow Ca(OH)Cl + H_2O$$
$$2\,HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\,H_2O$$

The compound $Ca(OH)Cl$ is intermediate between a salt and a base; it is therefore termed a *basic salt.* When dissolved in water it gives the hydroxyl ion characteristic of a base as well as the typical salt ions.

Extent of ionization. The question will naturally arise, When an acid, base, or salt dissolves in water, do all the molecules ionize or only some of them? The experiments by which this question is answered cannot be described here. It has been found, however, that only a fraction of the molecules ionize. The percentage which ionizes in a given case depends upon several conditions, the chief of which are as follows:

1. *The concentration of the solution.* In concentrated solutions only a very small percentage of the molecules ionize. As the solution is diluted the percentage increases, and in dilute solutions it may be very large, though it is never complete in any ordinary solution. Moreover, an acid such as sulfuric acid may form different ions according to the concentration of the solution:

$$H_2SO_4 \text{ (concentrated solution)} \longrightarrow H^+,\ HSO_4^-$$
$$H_2SO_4 \text{ (dilute solution)} \longrightarrow H^+,\ H^+,\ SO_4^{--}$$

2. *The nature of the dissolved compound.* At equal concentrations, substances differ much among themselves in percentage of ionization. Most salts are about equally ionized. Acids and bases, on the contrary, show great differences, some being freely ionized, others very slightly.

Strength of acids and bases. Since acid and basic properties are due to hydrogen ions and hydroxyl ions, the acid or base which will produce the greatest percentage of these ions at a given concentration must be regarded as the strongest representative of its class. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half of the molecules are dissociated into ions, and this is also approximately the extent to which most salts are ionized at this same concentration.

Methods of expressing reactions between compounds in solution. Chemical equations representing reactions between substances in solution may represent the details of the reaction, or they may simply indicate the final products formed. Thus, if we wish to call attention to the details of the reaction between sodium hydroxide and hydrochloric acid in solution, representing the ions which take part in the reaction, we write the equation as follows:

$$\mathrm{Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O}$$

If we wish simply to represent the substances taking part in the reaction and the final products formed, we write the equation thus:

$$\mathrm{NaOH + HCl \longrightarrow NaCl + H_2O}$$

Similarly, the two ways of expressing the reaction between zinc and hydrochloric acid are

$$\mathrm{Zn + 2\,(H^+, Cl^-) \longrightarrow Zn^{++}, (Cl^-)_2 + H_2}$$
$$\mathrm{Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2}$$

Radicals. We have seen that sulfuric acid as well as its salts all contain the group of atoms (SO_4). This group acts as a unit and forms an ion when the acid or its salts are dissolved in water. Similarly, nitric acid and its salts contain the group (NO_3), while all bases contain the group (OH). All such groups as these, which act as a unit in chemical reactions, are known as *radicals.* We may define a radical, therefore, as *a group of elements which act together as a unit in chemical reactions.* Many of these radicals have been given special names; for example, the radical (OH) is known as the hydroxyl radical.

Names of acids, bases, and salts. Since acids, bases, and salts are so intimately related to each other, it is very advantageous to give names to the three classes in accordance with some fixed system. The system universally adopted is as follows:

Naming of bases. All bases are called *hydroxides.* They are distinguished from each other by prefixing the name of the element which is in combination with the hydroxyl group. Examples: sodium hydroxide $(NaOH)$; calcium hydroxide, $Ca(OH)_2$; copper hydroxide, $Cu(OH)_2$.

Naming of acids. The method of naming acids depends upon whether the acid consists of two elements or three.

1. ***Binary acids.*** Acids containing only one element in addition to hydrogen are called *binary acids.* They are given names consisting of the prefix *hydro-*, the name of the second element present, and the termination *-ic.* Examples: hydrochloric acid (HCl); hydrosulfuric acid (H_2S).

2. ***Ternary acids.*** In addition to the two elements present in binary acids, the great majority of acids also contain oxygen. They therefore consist of three elements and are called *ternary acids.* It usually happens that the same three elements can unite in different proportions to make several different acids. The most familiar one of these is given a name ending in the suffix *-ic*, while the one with less oxygen is given a similar name, but ending in the

suffix *-ous*. Examples: nitric acid (HNO_3); nitrous acid (HNO_2). In cases where more than two acids are known, use is made of prefixes in addition to the two suffixes *-ic* and *-ous*. Thus the prefix *per-* signifies an acid still richer in oxygen; the prefix *hypo-* signifies one with less oxygen.

Naming of salts. A salt derived from a binary acid is given a name consisting of the names of the two elements composing it, with the termination *-ide*. Example: sodium chloride ($NaCl$). All other binary compounds are named in the same way.

A salt of a ternary acid is named in accordance with the acid from which it is derived. A ternary acid whose name has the termination *-ic* gives a salt with the name ending in *-ate*, while an acid with the termination *-ous* gives a salt with the name ending in *-ite*. The following table will make the application of these principles clear:

ACID	FORMULA	SALT	FORMULA
Hydrochloric	HCl	Sodium chloride	$NaCl$
Hypochlorous	$HClO$	Sodium hypochlorite	$NaClO$
Chlorous	$HClO_2$	Sodium chlorite	$NaClO_2$
Chloric	$HClO_3$	Sodium chlorate	$NaClO_3$
Perchloric	$HClO_4$	Sodium perchlorate	$NaClO_4$

Electrochemical series. Upon bringing a piece of zinc into a solution of an acid, zinc passes into solution and hydrogen is evolved:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate $CuSO_4$, zinc passes into solution, and a corresponding quantity of copper is precipitated:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

On the other hand, copper has no effect upon a solution of zinc sulfate.

It has been found to be possible to arrange hydrogen and the metals in a table in such a way that any element in the list will displace any one below it from its salts and will in turn be displaced from its salts by any one above it. This list is called the *electrochemical series* or the *displacement series.*

ELECTROCHEMICAL SERIES

1. Cæsium
2. Rubidium
3. Potassium
4. Sodium
5. Lithium
6. Calcium
7. Magnesium
8. Aluminium
9. Manganese
10. Zinc
11. Chromium
12. Cadmium
13. Iron
14. Cobalt
15. Nickel
16. Tin
17. Lead
18. Hydrogen
19. Arsenic
20. Copper
21. Antimony
22. Bismuth
23. Mercury
24. Silver
25. Platinum
26. Gold

This table enables us to foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts:

$$Mg + SnCl_2 \longrightarrow MgCl_2 + Sn$$

We should not, however, expect iron to displace aluminium.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from acids, while those below it will not. In the latter case, if any action takes place it must be preceded by oxidation.

From the standpoint of modern electrical theory this list really represents the relative ease with which the various atoms give up one or more electrons to form ions. Cæsium, the metal going into solution most readily, parts with an electron most easily, while such metals as gold and platinum retain their normal number of electrons most tenaciously.

EXERCISES

1. What are the salts of nitric acid called? the salts of sulfuric acid?

2. Name the acids represented by the following formulas: H_2SO_4, H_2SO_3, H_2SO_2, HNO_3, HNO_2.

3. Give the name of each of the compounds represented by the following formulas and tell to which group of compounds each belongs: $Mg(OH)_2$, HBr, $NaBr$, H_2SO_3, $CaSO_3$, $PbSO_4$, HI, $NaNO_2$, KNO_3, H_2CO_3, Na_2CO_3, $FeCl_3$.

4. 25 cc. of a solution containing 40 g. of sodium hydroxide per liter was found to neutralize 25 cc. of a solution of hydrochloric acid. What was the strength of the acid solution expressed in grams per liter?

5. After neutralizing a solution of sodium hydroxide with nitric acid, there remained after evaporation 100 g. of sodium nitrate. What weight of each compound had been used?

6. A solution contains 18 g. of hydrogen chloride per 100 cc. It required 25 cc. of this solution to neutralize 30 cc. of a solution of sodium hydroxide. What was the strength of the sodium hydroxide solution expressed in grams per 100 cc.?

7. When perfectly dry sulfuric acid (hydrogen sulfate) is treated with perfectly dry sodium hydroxide, no chemical change takes place. Explain.

8. When cold concentrated sulfuric acid is added to zinc, no change takes place. Recall the action of dilute sulfuric acid on the same metal. How do you account for the difference?

9. A solution of hydrogen chloride in benzene does not conduct the electric current. When this solution is treated with zinc, will hydrogen be evolved? Explain.

10. (*a*) Write equation for preparation of hydrogen from zinc and dilute sulfuric acid. (*b*) Rewrite the same equation from the standpoint of the theory of electrolytic dissociation. (*c*) Subtract the common ion (SO_4) from both members of the equation. (*d*) From the resulting equation, explain in what the preparation of hydrogen consists when examined from the standpoint of this theory.

11. In the same manner as in the preceding exercise, explain in what the action of sodium on water to give hydrogen consists.

CHAPTER XVII

VALENCE

Definition of valence. A comparison of the composition of the compounds of hydrogen with the other elements brings to light an interesting fact illustrated in the formulas

HCl	H_2O	H_3N	H_4C
(hydrogen chloride)	(water)	(ammonia)	(marsh gas)

It will be seen that the various kinds of atoms differ among themselves in the number of hydrogen atoms that they are able to hold in combination. An atom of chlorine combines with but one hydrogen atom, an atom of oxygen with two, one of nitrogen with three, and one of carbon with four. It is convenient to have a name to designate *that property of an element that determines the number of hydrogen atoms that its atom can hold in combination.* It is called the *valence* of an element.

Variety in valence. One atom of hydrogen never combines with more than one atom of any other kind, so that hydrogen is said to have a valence of 1, or to be *univalent.* Other elements, such as chlorine, iodine, and sodium, which combine with hydrogen atom for atom (HCl, HI, HNa), are likewise said to be univalent. On the other hand, elements such as oxygen, sulfur, and calcium, one atom of which combines with two atoms of hydrogen or of other univalent elements, are said to be *bivalent.* Similarly, we have *trivalent* elements, such as nitrogen; and *quadrivalent* ones, such as carbon. No element is known whose valence exceeds 8, and with most elements it does not exceed 4.

How elements of different valences combine. If the valence of two elements is the same, we may expect them to combine atom for atom. Thus the univalent elements, hydrogen and chlorine, combine to form the compound HCl; the bivalent elements, calcium and oxygen, to form the compound CaO; the trivalent elements, nitrogen and aluminium, to form AlN. When the valences of two elements are different, the ratio between the atoms is not so simple. The sum of the valences of the one kind of atoms in the molecule must equal the sum of the valences of the other kind of atoms; and this will require the two kinds of atoms to be present in unequal numbers. For example, bivalent calcium and univalent chlorine will give the compound $CaCl_2$; trivalent aluminium and univalent chlorine will give $AlCl_3$; trivalent iron and bivalent oxygen will give Fe_2O_3; quadrivalent carbon and bivalent oxygen will give CO_2.

Hydrogen and oxygen the standards for valence. It will be noticed that the fact that two elements combine in the ratio of 1 atom each, as in CaO, does not necessarily indicate that these elements are univalent. The hydrogen atom is taken as the standard, and *with it* calcium forms the compound CaH_2 and is therefore bivalent. Consequently in the compound CaO calcium as well as oxygen is bivalent.

Since the oxides of the elements are much better known than the hydrides, we often determine the valence of an element by examining the formula of its oxide rather than that of its hydride. As is indicated by the formula H_2O, oxygen is bivalent. Consequently from the formulas Na_2O, CaO, Al_2O_3 we infer that sodium (Na) is univalent; calcium (Ca) is bivalent; and aluminium (Al) is trivalent.

Probable formulas from known valences. If we know the valences of two elements, we can determine the probable formula which at least one of their compounds will have.

Thus, if we know that bromine (Br) is univalent (as is shown by the formula HBr) and that aluminium is trivalent, we may expect that the formula of aluminium bromide will be $AlBr_3$; if phosphorus (P) is pentavalent and oxygen is bivalent, phosphoric oxide will have the formula P_2O_5.

Valence of radicals. We have found that sometimes a group of atoms or a radical takes part in a reaction very much as though it were an atom (p. 188). It is very convenient to think of such a radical as having a valence like an element. Accordingly, from the formula $H(OH)$ or $Na(OH)$ we argue that the hydroxyl radical is univalent. Since calcium is bivalent, the formula of calcium hydroxide will therefore be $Ca(OH)_2$. From the formula $H_2(SO_4)$ we argue that the radical (SO_4) is bivalent; calcium sulfate should therefore have the formula $CaSO_4$ and aluminium sulfate the formula $Al_2(SO_4)_3$.

The replacing power of atoms and radicals. Just as elements having the same valence combine with each other atom for atom, so, if they replace each other in a chemical reaction, they will do so in the same ratio. Thus, one atom of bivalent zinc displaces two atoms of univalent hydrogen, as is shown in the following equations:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Zn(OH)_2 + H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O$$

Similarly, one atom of bivalent calcium displaces one atom of bivalent zinc:

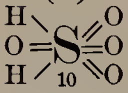
$$CaCl_2 + ZnSO_4 \longrightarrow CaSO_4 + ZnCl_2$$

Since many reactions, like those above, consist in the interchange of two elements, it is evident that a knowledge of the valence of the elements will assist us in writing the equations for the reactions.

Variable valence. It often happens that two given elements form more than one compound, and in such cases at least one of the elements must have more than one valence. We consider oxygen to be almost always bivalent, so that in the oxide CO carbon must be bivalent, while in the oxide CO_2 it is quadrivalent. Similarly, in the oxides FeO and Fe_2O_3 iron is bivalent and trivalent respectively. In general, it is true that each element has one valence that is much more frequently exerted than any other, so that we can think of a given element as having in the main a certain valence and less frequently some other valence.

Valence and structure of molecules. When a compound contains more than two elements, as H_2SO_4, it is not practicable to determine the valence of the several atoms from the formula, for we cannot tell in what way the elements are combined. If we make use of lines drawn between the symbols of the atoms to indicate valence as well as the relation of the atoms, the formula of water might be written H—O—H. This would mean that each hydrogen atom is univalent, while the oxygen is bivalent; and also that each hydrogen atom is in combination with the oxygen atom. Similarly, we might write the formula for sulfuric acid in a number of different ways, all of which would show the hydrogen to be univalent and the oxygen bivalent, yet the valence of sulfur might be different in each formula. In the following formulas the possible valences of sulfur are indicated by the numerals placed below the symbols:

(*A*)



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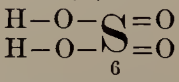
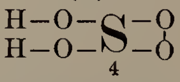
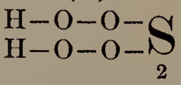


(*C*)

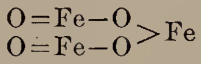


(*D*)



We should have to know which of these formulas expresses the truth before we could infer the valence of sulfur in the compound. Experiments indicate that the arrangement of the atoms represented in formula (*B*) is the correct one, so that the sulfur in sulfuric acid is hexavalent. Formulas like the ones just given, which represent the arrangement of the atoms in the molecule, are called *structural formulas.*

Even in compounds containing but two elements it is not always possible to draw correct conclusions from the mere formula. Thus, in the formula for magnetic oxide of iron (Fe_3O_4), if we assume oxygen to have its usual valence of 2, the four atoms will give a total of 8. If the three atoms of iron are all directly united with oxygen in the same way, then each atom of iron would have a valence of $2\frac{2}{3}$. It can be shown, however, that the structural formula of the oxide is as follows:



$$\left.\begin{matrix}\mathrm{O{=}Fe{-}O} \\ \mathrm{O{=}Fe{-}O}\end{matrix}\right>\mathrm{Fe}$$

It will be seen that two of the atoms of iron in the oxide are trivalent, while the other one is bivalent.

The cause of valence. If it be asked, Why do atoms differ in valence so that one atom of chlorine can combine with but one of hydrogen, while one of oxygen can combine with two? the answer will have to be that we do not know. It seems probable, however, that the cause is to be found in the capacity of atoms of the various elements to take up different charges of electricity.

We have seen that the electrical charges on the ions of an electrolyte in solution are always multiples of a single unit charge. Thus, with hydrogen chloride the ions formed have each a unit charge, one ion being plus (+), the other minus (−):

$$\mathrm{HCl} \longrightarrow \mathrm{H}^+ + \mathrm{Cl}^-$$

This corresponds to the fact that hydrogen and chlorine are univalent. With calcium sulfate we have the equation

$$CaSO_4 \longrightarrow Ca^{++} + SO_4^{--}$$

The double charge corresponds to the bivalency of calcium and of the radical (SO_4).

It seems to be probable that a similar explanation holds good for valency in general. If a given atom tends to take up three positive charges, it will have a valence of three, like aluminium, and will tend to combine with atoms or radicals having negative charges. If it takes up two negative charges, it will have a valence of two, like oxygen, and will tend to combine with atoms or radicals having positive charges. These facts lead us to speak of elements as either *electropositive* or *electronegative*. When charged atoms unite they form molecules consisting of the two kinds of atoms, and in such ratios that the positive charge of the one just neutralizes the negative charge of the other.

Table of valences. It will be convenient for reference to tabulate the valences of the most familiar elements and radicals and the number of charges they carry as ions. Some elements will be found in several different lines, since they have more than one valence.

TABLE OF VALENCES

VALENCE	POSITIVE IONS	NEGATIVE IONS	NOT IONS
1	H, Na, K, Ag, NH_4	Cl, Br, I, OH, NO_3	
2	Ca, Ba, Mg, Zn, Hg, Cu, Fe, Sn	S, SO_4, CO_3	O
3	Al, Bi, Sb, Fe	PO_4	N, P
4	Sn	SiO_4	C, Si, S
5			N, P, As, Sb
6			S

EXERCISES

1. In the compounds whose formulas follow, the valence of one of the elements is indicated by a figure placed over the symbol. What is the valence of each of the other elements or radicals present in the compounds?

$$\overset{2}{Mg}Br_2;\ \overset{2}{Ca}O;\ \overset{2}{Ca}(OH)_2;\ \overset{2}{Ba}_3(PO_4)_2;\ \overset{1}{K}NO_3;\ \overset{1}{H}_2O$$

Verify your results by reference to the table.

2. Complete and balance the following equations, assuming that in each instance the sodium or the calcium in the first compound changes place with the hydrogen of the second:

$$\begin{array}{r} NaOH + HCl \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \\ NaOH + H_2SO_4 \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \\ NaOH + H_3PO_4 \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \\ Ca(OH)_2 + HCl \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \\ Ca(OH)_2 + H_2SO_4 \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \\ Ca(OH)_2 + H_3PO_4 \longrightarrow \_\_\_\_\_ + \_\_\_\_\_ \end{array}$$

3. Sodium, calcium, and aluminium have valences of 1, 2, and 3 respectively; write the formulas of their chlorides, sulfates, and phosphates (phosphoric acid = H_3PO_4), on the supposition that they form salts having the normal composition.

4. Iron forms one series of salts in which it has a valence of 2, and another series in which it has a valence of 3; write the formulas for the two chlorides of iron, also for the two sulfates, on the supposition that these have the normal composition.

5. Silver acts as a univalent element and calcium as a bivalent element in the formation of their respective nitrates and chlorides. (*a*) Write the formula for silver nitrate; for calcium chloride. (*b*) When solutions of these two salts are mixed, the two metals, silver and calcium, exchange places; write the equation for the reaction.

6. Antimony acts as a trivalent element in the formation of a chloride. (*a*) What is the formula for antimony chloride? (*b*) When hydrogen sulfide (H_2S) is passed into a solution of this chloride, the hydrogen and antimony exchange places; write the equation for the reaction.

CHAPTER XVIII

COMPOUNDS OF NITROGEN

Occurrence. Large quantities of nitrogen occur in the atmosphere, and it is substantially all in the free state. In the materials composing the earth's crust, on the other hand, there occur in certain localities considerable deposits of compounds of nitrogen, especially of sodium nitrate ($NaNO_3$). Moreover, such compounds are present, at least in small quantities, in all productive soils. From these soils the nitrogen is taken up by plants and built into complex compounds. Animals feeding on these plants assimilate the nitrogenous matter, which becomes an essential part of the animal tissue. In both plants and animals the nitrogen is present chiefly in the form of proteid matter, which consists of complex compounds containing the elements carbon, nitrogen, oxygen, and hydrogen, and sometimes phosphorus and sulfur.

The unstable character of compounds of nitrogen. Experiment shows that the molecule of nitrogen has the formula N_2 and that the element is very inactive at ordinary temperatures. This inactivity seems to be partly due to the fact that the nitrogen molecule is very stable and that a good deal of energy is required to separate it into its atoms, which must be done before it can enter into combination with other elements. On the other hand, when nitrogen occurs as a constituent of a compound, the nitrogen atoms tend to leave the compound, with liberation of energy, and form stable nitrogen molecules. As a result of this tendency compounds containing nitrogen are apt to be unstable. It is largely due to the unstable character of certain nitrogenous compounds that they are so extensively used as a constituent of explosives.

While a great many compounds of nitrogen are known, it is desirable at this time to become acquainted with only some of the simple ones, especially those which nitrogen forms with hydrogen and with oxygen.

COMPOUNDS OF NITROGEN WITH HYDROGEN

Nitrogen forms three simple compounds with hydrogen, the names and formulas of which are as follows: ammonia (NH_3), hydrazine (N_2H_4), and hydronitric acid (HN_3). Of these ammonia is by far the most important.

Ammonia. Inasmuch as ammonia is formed in certain natural processes which are constantly taking place about us, such as the decay of nitrogenous organic matter, it is easy to understand why this compound has been known for so long a time. It was originally prepared by heating such tissues as the hoofs and horns of animals, and the aqueous solution of the gas so obtained was termed *spirits of hartshorn.* The pure gas itself was first prepared by Priestley, in 1774, and its composition was determined soon after by the French chemist Berthollet.

Preparation of ammonia. The principal methods for preparing ammonia are as follows:

1. ***Laboratory method.*** In the laboratory, ammonia is usually prepared from ammonium chloride (NH_4Cl), a white solid obtained in the manufacture of coal gas. When a mixture of ammonium chloride and sodium hydroxide is heated, the ammonium radical (NH_4) and sodium change places, as represented in the following equation:

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$$

The resulting ammonium hydroxide (NH_4OH) is unstable and, as fast as it is formed, breaks down into water and ammonia:

$$NH_4OH \longrightarrow NH_3 + H_2O$$

Calcium hydroxide, $Ca(OH)_2$, is frequently used in place of the more expensive sodium hydroxide:

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\,NH_4OH$$
$$2\,NH_4OH \longrightarrow 2\,H_2O + 2\,NH_3$$

The ammonium chloride and calcium hydroxide are mixed together and placed in a flask *A*, arranged as shown in Fig. 84. The mixture is gently warmed, when ammonia is evolved as a gas and, being much lighter than air, is collected in *B* by displacement of air, as shown in the diagram.

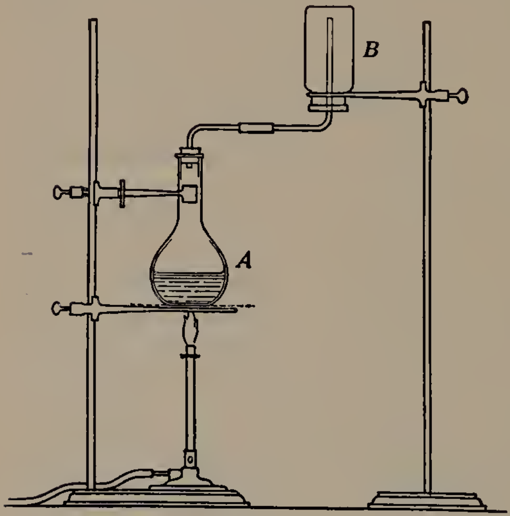


Fig. 84. The preparation and collection of ammonia in the laboratory

2. ***Commercial preparation.*** Ammonia is obtained commercially in the process of manufacturing coal gas and coke. Certain grades of soft coal are best adapted for this purpose. Such coal contains, in addition to carbon, about 1 per cent of nitrogen and 7 per cent of hydrogen, as well as small percentages of other elements. When such coal is heated in retorts from which the air is excluded (p. 306), complicated changes take place, resulting not only in the formation of the combustible gases which constitute coal gas but also

of ammonia and many other valuable products. From 25 to 50 per cent of the nitrogen present in the coal is converted into ammonia. The volatile matter expelled from the coal is passed through water, which absorbs the ammonia, together with certain other compounds, forming a solution known as the *ammoniacal liquor*. When this liquor is heated with slaked lime, ammonia is evolved and is absorbed either in water or in a dilute solution of an acid.

3. ***The synthetic method (the Haber process).*** Ammonia may be formed by the direct union of nitrogen and hydrogen. The best yield is obtained when a mixture of the gases, subjected to a pressure of 200 atmospheres, is heated to about 500° in contact with finely divided iron, which acts as a catalytic agent. Under these conditions, a small percentage of ammonia is formed. The gases are then passed through water, which dissolves the ammonia, while the nitrogen and hydrogen mixture is again conducted over the heated iron. The process thus becomes continuous, more nitrogen and hydrogen being introduced as needed. This process, known as the Haber process from the German chemist who devised it, is now used to a certain extent in Germany for the production of ammonia on a large scale.

Ammonia is likewise formed when an electric discharge is passed through a mixture of nitrogen and hydrogen, but the yield is very small.

Properties. Ammonia is a colorless gas having a strong, suffocating odor. Under standard conditions 1 l. of the pure gas weighs 0.7708 g., being 0.59 times as heavy as air. The gas is easily condensed to a colorless liquid boiling at – 33.5°, and in this form is an article of commerce. Liquid ammonia, like water, is not only an excellent solvent but also a highly ionizing one. Ammonia can be obtained in the form of a snowlike solid melting at – 75.5°.

Ammonia is extremely soluble in water, 1 l. of water at 0° and 760 mm. pressure dissolving 1298.9 l. of the gas, and 710 l. at 20°. In dissolving such large volumes of the gas the water expands considerably, so that the density of the solution is less than that of water. The most concentrated commercial solutions have a density of 0.88, and contain 35.6 per cent by weight of the gas.

Chemical conduct. At ordinary temperatures ammonia is a stable compound. When heated to high temperatures, however, or when subjected to the action of an electric discharge, it is decomposed into its elements. It will burn in an atmosphere of oxygen, but not in air unless heat is continuously applied.

The hydrogen of ammonia can be displaced by metals forming *nitrides.* Thus, magnesium forms the white solid magnesium nitride (Mg_3N_2):

$$3\,Mg + 2\,NH_3 \longrightarrow Mg_3N_2 + 3\,H_2$$

It will be observed that the decomposition of ammonia by heating is just the reverse of the formation of ammonia in the Haber process. These reactions will be discussed in Chapter XIX.

Action of ammonia upon water; ammonium hydroxide. The solution of ammonia in water, called *aqua ammonia,* is found to have strong basic properties. It turns red litmus blue; it feels soapy to the touch; it neutralizes acids, forming salts with them. It seems certain, therefore, that when ammonia dissolves in water, a portion of the gas combines chemically with water according to the equation

$$NH_3 + H_2O \longrightarrow NH_4OH$$

It is the substance NH_4OH, called *ammonium hydroxide,* which has the basic properties, dissociating into the ions NH_4^+ and OH^-. At ordinary temperatures the separation of the pure hydroxide from its solutions has not been accomplished, for as the solution becomes concentrated the compound decomposes again into ammonia and water.

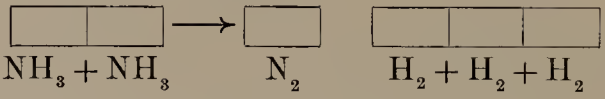
Ammonium salts. When an acid is added to aqua ammonia, the ammonium hydroxide and the acid neutralize each other according to the following equations:

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$
$$2\,NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2\,H_2O$$

Upon evaporation the resulting salts, NH_4Cl and $(NH_4)_2SO_4$, are obtained in the form of white solids. In these salts the radical NH_4 plays the part of a metal. On this account the name *ammonium* is given to it, since the names of most of the metals end in *ium*. Salts containing this radical are known as *ammonium salts*. Some of the most common of these salts are ammonium chloride (NH_4Cl), ammonium sulfate, $(NH_4)_2SO_4$, and ammonium nitrate (NH_4NO_3).

Uses of ammonia. Large quantities of ammonia are used in the manufacture of aqua ammonia, as well as in the formation of ammonium compounds, such as ammonium chloride and ammonium sulfate. In the liquid state it is also used extensively in the manufacture of artificial ice (p. 110). Its use for this purpose is based on the facts that the gas is easily liquefied by pressure and that the resulting liquid has a relatively high heat of vaporization.

Composition of ammonia. That ammonia is a compound of nitrogen and hydrogen is proved by the fact that it may be formed by the direct union of the two elements (see method of preparation). The quantitative composition of the compound may be determined by taking advantage of certain reactions which make it possible to liberate the nitrogen as well as the hydrogen from any definite volume of ammonia. By measuring the volumes of the gases so liberated one can compare them not only with each other but also with the volume of the ammonia from which they were derived. In this way it has been proved that 2 volumes of ammonia yield on decomposition 1 volume of nitrogen and 3 volumes of hydrogen, as expressed graphically in the following equation:



$$NH_3 + NH_3 \longrightarrow N_2 \quad H_2 + H_2 + H_2$$

Hydrazine (N_2H_4). This is a colorless liquid boiling at 113.5°. Like ammonia, it combines with water to form a base, from which salts can be prepared by the action of acids.

Hydronitric acid (HN_3). This acid is a colorless liquid of disagreeable odor. It boils at 37° and is violently explosive, decomposing into its constituent elements with the liberation of considerable heat. The salts of hydronitric acid are solids. Some of them are violently explosive and are used in the manufacture of explosives.

Compounds of Nitrogen with Hydrogen and Oxygen

Nitrogen forms a number of compounds with hydrogen and oxygen, the most important of which are the two acids, nitric acid (HNO_3) and nitrous acid (HNO_2).

Nitric acid. Nitric acid was well known to the alchemists, being first prepared by the Egyptians. In the ninth century the alchemist Geber prepared it from saltpeter (KNO_3) by a process somewhat similar to that used at the present time, and the Germans still call it *salpetersäure*. The composition of the acid was first determined by Lavoisier and Priestley.

Because of its great activity nitric acid does not occur free in nature, but a number of its salts are found in considerable quantities. The most abundant of these is sodium nitrate ($NaNO_3$), which is found in large quantities in Chile and is known as Chile saltpeter.

Preparation of nitric acid. Nitric acid can be prepared by a number of different methods, the most important of which are the following:

1. ***Preparation from sodium nitrate.*** When sodium nitrate is treated with concentrated cold sulfuric acid, no chemical action seems to take place. If, however, the mixture is placed in a retort *A* (Fig. 85) and a gentle heat applied, nitric acid is given off as a vapor and may be condensed to a liquid by conducting the vapor into a tube *B* surrounded by ice water, as shown in Fig. 85. An examination of the liquid left in the retort shows that it contains acid sodium sulfate ($NaHSO_4$), half of the hydrogen of sulfuric acid having been replaced by sodium. The equation for the reaction is as follows:

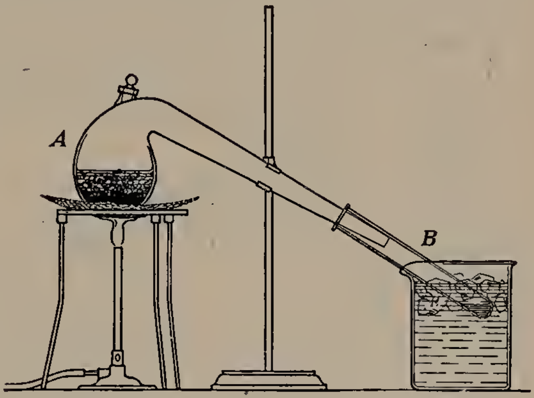


FIG. 85. The preparation of nitric acid in the laboratory

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

If a smaller quantity of sulfuric acid is taken and the mixture is heated to a high temperature, normal sodium sulfate is formed:

$$2\,NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HNO_3$$

In this case, however, the higher temperature required decomposes a part of the nitric acid, so the process is not economical.

The commercial preparation of nitric acid. Fig. 86 illustrates a form of apparatus used in the preparation of nitric acid on a large scale. Sodium nitrate and sulfuric acid are heated in the iron retort *A*. The resulting acid vapors pass in the direction indicated by the arrows, and are condensed in the glass tubes *B*, which are covered with cloth kept cool by streams of water. These tubes are inclined so that the liquid resulting from the condensation of the vapors runs back into *C* and is drawn off into large vessels (*D*).

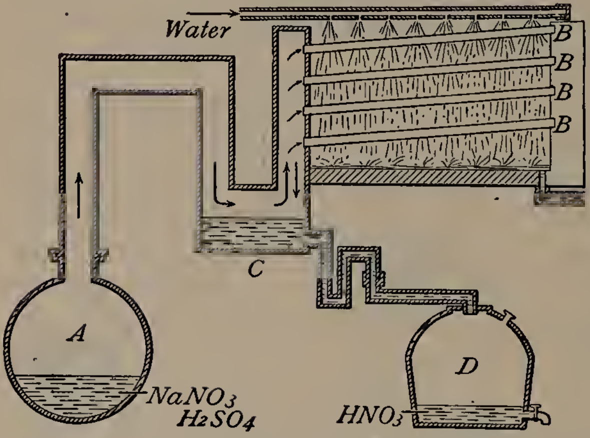


FIG. 86. A commercial still for the production of concentrated nitric acid

2. ***Preparation from air.*** When an electric discharge takes place through a mixture of oxygen and nitrogen (air), a small percentage of oxides of nitrogen is formed. This can be increased by having the mixture pass through an electric arc which has been drawn out to a great size by magnets (Fig. 87). The oxides so obtained combine with water to form dilute nitric acid. This method for preparing nitric acid (known as the Birkeland and Eyde process) has come into extensive use in recent years in Norway, since the necessary electrical energy can be generated at a very low cost by the waterfalls abounding in that country. The dilute nitric acid obtained is neutralized with lime (CaO), and the resulting calcium nitrate is sold for use as a fertilizer under the name *air saltpeter*.

3. *Preparation from ammonia.* Nitric acid is also formed by the oxidation of ammonia. The process consists in heating a mixture of ammonia and air in contact with platinum or some other catalyzer.

The preparation of nitric acid from sodium nitrate is, under normal conditions, the most economical process. The methods used in its preparation from air and from ammonia, however, are coming into use and undoubtedly will displace the sodium nitrate method as the supply of this salt becomes exhausted. During the great war the Central Powers could not obtain sodium nitrate and hence prepared the enormous supplies of nitric acid required in the manufacture of explosives chiefly from ammonia.

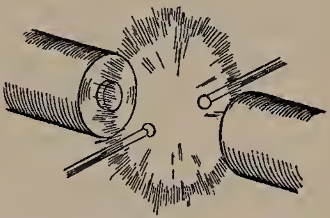


Fig. 87. Form of the electric arc employed in the Birkeland and Eyde process

Properties of nitric acid. Pure nitric acid (hydrogen nitrate) is a colorless liquid which boils at about 86° and has a density of 1.56. The concentrated acid of commerce contains about 68 per cent of the acid, the remainder being water. Such a mixture has a density of 1.4. The concentrated acid fumes somewhat in moist air, and has a sharp, choking odor.

Chemical conduct. The most important chemical reactions of nitric acid are the following:

1. *Acid action.* Nitric acid has all the characteristics of a *strong* acid. It changes blue litmus red, and has a sour taste in dilute solutions. It gives the ions H^+ and NO_3^- in solution, and neutralizes bases, forming salts. It also acts upon the oxides of most metals, forming a salt and water; thus,

$$CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

2. ***Decomposition on heating.*** When nitric acid is boiled or when it is exposed for some time to sunlight, it suffers a partial decomposition according to the equation

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2$$

The substance NO_2 (called nitrogen dioxide) is a brownish gas which is readily soluble in water and in nitric acid. It therefore dissolves in the undecomposed acid, and imparts to it a yellowish or reddish color. Concentrated nitric acid highly charged with this substance is called *fuming nitric acid.*

3. ***Oxidizing action.*** Because of its easy decomposition, nitric acid is a good oxidizing agent. Under ordinary circumstances, when acting as an oxidizing agent, it is decomposed according to the equation

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO + 3\,[O]$$

The oxygen is taken up by the substance oxidized and is not set free, which fact is indicated in the equation by placing the symbol for oxygen in brackets. Thus, if carbon is oxidized by nitric acid, the oxygen combines with carbon, forming carbon dioxide (CO_2):

$$C + 2\,[O] \longrightarrow CO_2$$

4. ***Action upon metals.*** All of the metals, with the exception of gold, platinum, and a few of the rare metals, are acted upon more or less readily by nitric acid. The action may be regarded as taking place in two different ways, depending upon the metal and the concentration of the acid.

(a) *Metals occurring above hydrogen in the electrochemical series.* It will be recalled that those metals occurring above hydrogen in the electrochemical series liberate hydrogen from dilute acids. Experiments show, however, that when these metals are dissolved in nitric acid, hydrogen, if evolved at all, is evolved only when the acid is very dilute. In place of hydrogen certain reduction products of nitric acid are formed, most frequently nitric oxide, a gas having the formula NO. A little reflection will show that this is just what we might expect, for hydrogen is a strong reducing agent, while nitric acid is an equally strong oxidizing agent. Accordingly, if hydrogen were to be liberated in contact with nitric acid, it would not be evolved as such, but would at once react with the acid, probably in the following manner:

$$HNO_3 + 3\,H \longrightarrow 2\,H_2O + NO$$

In all such cases the complete reaction taking place may be illustrated by the following equations representing the reaction between zinc and nitric acid (the expression 2 [H] indicates that the hydrogen formed is not liberated as such, but as fast as formed reacts according to equation (2)):

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + 2\,[H] \qquad (1)$$
$$3\,[H] + HNO_3 \longrightarrow 2\,H_2O + NO \qquad (2)$$

In case the nitric acid is very concentrated, the nitric oxide is oxidized by the acid to form nitrogen dioxide, — a reddish-brown gas having the formula NO_2.

It is often convenient to express in a single equation a reaction that really takes place in steps such as that between zinc and nitric acid. This is readily done by combining equations (1) and (2) as given above. Before the equations are combined, however, they must be modified so as to express the fact that all the hydrogen represented as being formed according to equation (1) reacts with the nitric acid according to equation (2). This may be done by multiplying the first equation by 3 and the second equation by 2. The two equations will then be as follows:

$$3\,Zn + 6\,HNO_3 \longrightarrow 3\,Zn(NO_3)_2 + 6\,[H]$$
$$6\,[H] + 2\,HNO_3 \longrightarrow 4\,H_2O + 2\,NO$$

By canceling the common factor 6 [H], which represents the hydrogen formed in the one reaction and used up in the other, and then combining the equations, the following is obtained:

$$3\ Zn + 8\ HNO_3 \longrightarrow 3\ Zn(NO_3)_2 + 4\ H_2O + 2\ NO$$

This complete equation has the advantage of making it possible to calculate very easily the proportions in which the various substances enter into the reaction or are formed in it. It is unsatisfactory in that it does not give full information about the way in which the reaction takes place.

(b) *Metals occurring below hydrogen in the electrochemical series.* Those metals occurring below hydrogen in the electrochemical series, if acted upon by nitric acid at all, are first oxidized to the corresponding oxides. These oxides, as fast as formed, react with more acid to form the corresponding salt. Thus, with copper and nitric acid the reactions are represented by the following equations:

$$2\ HNO_3 \longrightarrow H_2O + 2\ NO + 3\ [O] \qquad (1)$$
$$3\ [O] + 3\ Cu \longrightarrow 3\ CuO \qquad (2)$$
$$3\ CuO + 6\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 3\ H_2O \qquad (3)$$

By canceling the factors 3 [O] and 3 CuO, which represent substances formed in one reaction and used up in another, and combining the three equations we get the following:

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

Uses of nitric acid. Nitric acid is used in very large quantities in the manufacture of explosives, of celluloid, and of dyes. It is a very important reagent in chemical laboratories.

Aqua regia. Since nitric acid is a good oxidizing agent, we might expect it to liberate chlorine from hydrogen chloride, and this is found to be the case. A mixture of

1 part of nitric acid and 3 parts of hydrochloric acid is called *aqua regia*, and is one of the strongest solvents known. It owes its solvent powers not to its acid properties, but to the nascent chlorine which it liberates. Metals such as gold and platinum, which are not soluble in any of the common acids, readily dissolve in aqua regia, being converted into chlorides by the nascent chlorine.

Salts of nitric acid; nitrates. The salts of nitric acid are called *nitrates*. Many of these salts will be described in the study of the metals. They are all soluble in water, and when heated to a high temperature, undergo decomposition. In a few cases a nitrate, on being heated, evolves oxygen, forming a *nitrite*:

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2$$

In most cases the decomposition goes farther, and the metal is left as an oxide:

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

The nitrates are especially used in the manufacture of gunpowder, sulfuric acid, nitric acid, and as a fertilizer.

Nitrous acid (HNO_2). It is an easy matter to obtain sodium nitrite ($NaNO_2$) by heating sodium nitrate, as explained in the previous paragraph. Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed and nitrous acid is set free:

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_2$$

The acid is very unstable, however, and decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of coal-tar dyes.

OXIDES OF NITROGEN

The most important of the oxides of nitrogen are the following:

Nitrous oxide (N_2O)	a colorless gas
Nitric oxide (NO)	a colorless gas
Nitrogen dioxide (NO_2) . . .	a reddish-brown gas
Nitrogen trioxide (N_2O_3) . .	stable only at low temperatures
Nitrogen tetroxide (N_2O_4) . .	a low-boiling, nearly colorless liquid
Nitrogen pentoxide (N_2O_5) . .	a white solid

Nitrous oxide (laughing gas) (N_2O). Nitrous oxide was first prepared by Priestley in 1772. Davy determined its composition in 1800 and was the first to point out the property which the gas possesses of rendering one temporarily unconscious when it is inhaled.

The most convenient method for its preparation consists in heating ammonium nitrate. Just as ammonium nitrite, when heated, yields water and nitrogen (p. 130), so ammonium nitrate decomposes in a similar way, forming water and nitrous oxide. The similarity between the two reactions is shown in the following equations:

$$NH_4NO_2 \longrightarrow 2\,H_2O + N_2$$
$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O$$

Nitrous oxide is a colorless gas somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled it produces a kind of hysteria (hence the name *laughing gas*) and, if taken in large amounts, insensibility to pain, and unconsciousness. It was the first substance to be used as an anesthetic in surgery and is still used in minor operations, such as those of dentistry.

Nitrous oxide is a very energetic oxidizing agent. Substances such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting nitrogen free. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

Nitric oxide. Nitric oxide is most readily prepared by the action of nitric acid (density, 1.2) upon certain metals below hydrogen in the electrochemical series, such as copper (p. 212).

The metal is placed in a flask *A* (Fig. 88) and the acid slowly added through the funnel tube *B*. The gas escapes through *C* and is collected over water. The gas at first evolved combines with the oxygen of the air contained in the flask to form the reddish-brown nitrogen dioxide, but this is dissolved as it bubbles through the water.

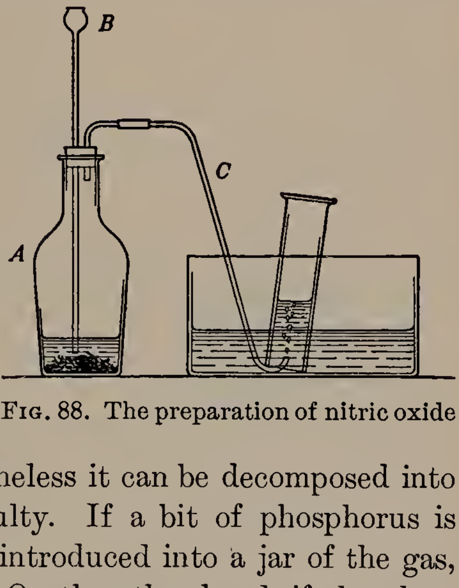


Fig. 88. The preparation of nitric oxide

Nitric oxide is a colorless gas slightly heavier than air. It is a much more stable compound than nitrous oxide; nevertheless it can be decomposed into its elements without difficulty. If a bit of phosphorus is barely ignited and at once introduced into a jar of the gas, the flame is extinguished. On the other hand, if the phosphorus is first heated until vigorous combustion ensues, and is then introduced into the gas, the combustion continues with great brilliancy.

When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen, even at ordinary temperatures, forming a reddish-brown gas, NO_2, which is called *nitrogen dioxide*:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

To show the formation of nitrogen dioxide from nitric oxide and oxygen, a tube is filled with the oxide, inverted in water, and pure oxygen is passed into it, as shown in Fig. 89. As each bubble of oxygen enters, it unites with the nitric oxide to form the reddish-brown dioxide. In a few minutes the color fades (because of the action of water upon the dioxide), and the water slowly rises in the tube.

Nitrogen dioxide (NO_2). This gas, as we have just seen, is formed by allowing nitric oxide to come into contact with oxygen. It can also be made by heating certain nitrates, such as lead nitrate (p. 213). It is a reddish-brown gas of unpleasant odor, and is poisonous when inhaled. It gives up a part of its oxygen to burning substances, acting as an oxidizing agent:

$$NO_2 \longrightarrow NO + [O]$$

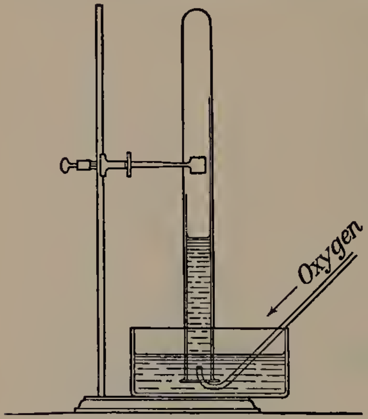


FIG. 89. The formation of nitrogen dioxide from nitric oxide and nitrogen

Nitrogen tetroxide. At lower temperatures nitrogen dioxide becomes paler in color and condenses to a pale-yellow liquid. It has been shown that this paler gas has the formula N_2O_4, and it is called *nitrogen tetroxide*. At ordinary temperatures the gas is a mixture of the two, and we may express this relation thus:

$$\underset{\text{high temperatures}}{\text{Nitrogen dioxide, } 2\,NO_2} \rightleftarrows \underset{\text{low temperatures}}{\text{nitrogen tetroxide, } N_2O_4}$$

Acid anhydrides. The oxides N_2O_3 (nitrogen trioxide) and N_2O_5 (nitrogen pentoxide) are rarely prepared and need not be separately described. They bear a very interesting relation to the acids of nitrogen. When dissolved in water they combine with the water and form acids:

$$N_2O_3 + H_2O \longrightarrow 2\,HNO_2$$
$$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$$

Many other oxides act in the same way, combining with water to form an acid. Such oxides are called *acid anhydrides.* An acid anhydride may therefore be defined as *an oxide that combines with water to form an acid.*

EXERCISES

1. Perfectly dry ammonia does not affect litmus paper. Explain.

2. Can ammonia be dried by passing the gas through concentrated sulfuric acid? Explain.

3. Ammonium hydroxide is a weak base; that is, it is not highly dissociated. When it is neutralized by strong acids, the heat of reaction is less than when strong bases are so neutralized. Suggest some possible cause for this.

4. Write the equations for the reactions taking place when ammonium hydroxide is neutralized by hydrochloric acid, by sulfuric acid, and by nitric acid respectively.

5. It is said that nitric acid is formed in the air during thunderstorms. How would you account for its formation?

6. What does the word *ammonia* mean? (Consult dictionary.)

7. Why is nitric acid said to be a strong acid?

8. What are the properties of ammonia that make it suitable for use in the preparation of artificial ice?

9. Write the equations representing the reactions between ammonium hydroxide and sulfuric acid and between ammonium hydroxide and nitric acid, in accordance with the theory of electrolytic dissociation.

10. State the compounds and ions present in aqua ammonia.

11. What is meant by the statement "the reaction between water and ammonia is a reversible reaction"?

12. Why is it necessary to apply heat in the preparation of nitric acid from sodium nitrate?

13. Give the steps in the production of nitric acid from air and water.

14. How many liters of ammonia at 0° and 760 mm. pressure will 1 l. of water dissolve? What would this volume of ammonia weigh? What weight of ammonium chloride would be necessary to prepare it?

15. (*a*) Calculate the weight of 1 l. of the concentrated nitric acid of commerce (p. 209). (*b*) What weight of hydrogen nitrate (HNO_3) will this contain? (*c*) What weights of materials (H_2SO_4 and $NaNO_3$) are necessary for its preparation?

16. How many liters of nitrous oxide, measured under standard conditions, can be prepared from 10 g. of ammonium nitrate?

17. What weight of copper is necessary to prepare 50 l. of nitric oxide?

18. What weight of sodium hydroxide is necessary to neutralize 1 l. of the concentrated nitric acid of commerce? Calculate the weight of the resulting compound.

19. 40 cc. of the concentrated nitric acid of commerce was added to 25 g. of zinc. After the reaction had ceased, the resulting mass was heated until the water present was all evaporated. Calculate the weight of the residue.

CHAPTER XIX

SPEED OF REACTIONS; EQUILIBRIUM

Speed of a reaction. If the reactions we have studied are attentively examined, it will be noticed that some go on very slowly, while others are very rapid. For example, Lavoisier found that tin must be heated in the air for days before an appreciable quantity of the oxide is formed (p. 4). So, too, the action of acids upon pure zinc is very slow. On the other hand, when iron and sulfur have been heated to the temperature at which noticeable action begins, the action proceeds very rapidly. We express these facts by saying that reactions differ greatly among themselves *in their speed.* By the speed of a reaction is meant the quantity of a given substance that undergoes change in a unit of time.

Factors that affect the speed of a reaction. A number of factors alter the speed at which a given reaction will take place.

1. *Temperature.* The most familiar way to hasten a reaction is to raise the temperature of the materials undergoing change. In ordinary combustion it is a familiar fact that the hotter the fire, the faster the coal burns, while at ordinary temperatures the coal does not seem to oxidize at all, though there is plenty of oxygen in contact with it. It is probable that even under these latter conditions there is some chemical action, but it is so slow that we cannot easily detect it. In general, it has been found that

a rise of 10° about doubles the speed of most reactions. Consequently, if we are in doubt as to whether two things can act upon each other, we gradually raise the temperature of the mixture, knowing that this will increase the speed of action if there is any taking place.

2. ***Concentration — mass action.*** It is evident that if we increase the quantity of oxygen in contact with the surface of a burning substance, we shall increase the speed of the combustion. For this reason substances burn much more rapidly in pure oxygen than in air, for the latter is only one fifth oxygen. The blacksmith pumps air into the forge to supply oxygen faster than it would be supplied by natural draft, and this operation amounts to increasing the quantity of oxygen available at any one time. We can express these facts by saying that the speed with which a given material burns depends upon the concentration of the oxygen. By *concentration* we mean the weight of oxygen present in a given volume of gas.

Instead of increasing the concentration of the oxygen, we may increase the surface of the burning substance. A log of wood burns more slowly than the same log split into kindling or worked into shavings. A lump of coal burns rather slowly; but when finely powdered and suspended in the air as dust, it burns almost instantaneously and with explosive violence. If we burn a given weight of coal in the air, we shall, of course, get a definite weight of product and use up a definite weight of oxygen. But if we force into contact with the coal much more oxygen than can be used, the coal burns much faster. This effect of the excess of oxygen is called *mass action.* In general, any reaction can be hastened by the effect of mass action; that is, by using a large excess of one of the reacting substances.

3. ***Catalysis.*** We have found that certain reactions go on much more rapidly in the presence of some material that does not seem to take any real part in the process, since it remains left over at the end. Such a substance is called a *catalyzer*, and its action is called *catalysis* (p. 26). Thus, at a given temperature potassium chlorate gives up oxygen more rapidly when manganese dioxide has been added to it than when the pure substance is heated (p. 26). Nitrogen combines with hydrogen much more rapidly in the presence of iron than in its absence (p. 203). A catalyzer reminds us of a lubricant in machinery. It makes the reaction proceed more rapidly, just as oil makes the machine run more easily.

Reversible reactions. We have met with a number of reactions that are especially interesting, because by changing the conditions we can make them go in either direction at will. Thus, when we heat mercuric oxide we obtain mercury and oxygen (p. 25), while if we heat mercury in contact with oxygen at a somewhat different temperature, we obtain mercuric oxide. These facts are represented in the following way:

$$2\,HgO \rightleftarrows 2\,Hg + O_2$$

In a similar way we have found that when an electric discharge is passed through a mixture of nitrogen and hydrogen we get a small quantity of ammonia, yet when the discharge is passed through ammonia we get a mixture of nitrogen and hydrogen (p. 204):

$$2\,NH_3 \rightleftarrows N_2 + 3\,H_2$$

When ammonia is dissolved in water we have every reason for thinking that ammonium hydroxide is formed (p. 204), yet when we attempt to evaporate the solution to obtain this compound, it decomposes into water and ammonia:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Reactions of this kind are called *reversible reactions.*

Equilibrium. If we remember that the materials taking part in a reaction are made up of a vast number of molecules, all of which are in motion at various speeds and are constantly changing their relations to each other, it will not be difficult to imagine why some molecules in a given mixture may be decomposing while others are being formed. Moreover, at the outset of the reaction the masses of the substances present tend to drive the reaction in one direction, while later, when the masses of the original substances have diminished, the masses of the substances formed have increased. If these latter are capable of reacting to form the original substances, the effect of mass will now be to drive the reaction in the reverse direction. In time a condition will be reached in which the changes taking place in the one direction will just offset those in the other. The *average percentage* of each material present will then remain unchanged, though the individual molecules will keep on changing. This condition of affairs is called *equilibrium.* Thus, ammonia, hydrogen, and nitrogen come to equilibrium in the presence of electric discharge when there is about 7 per cent of ammonia present, the percentage depending upon the temperature and the relative quantities of the gases originally mixed.

Effect of mass upon equilibrium. When equilibrium has been reached, suppose we add an additional quantity of one of the acting substances — say, hydrogen in the case just mentioned. This will enable the nitrogen to act more rapidly upon the hydrogen, for the two kinds of molecules will now meet more frequently. It will not at all affect the rate at which ammonia is decomposing, for this does not in any way depend upon the presence of hydrogen. The net effect will therefore be to bring about a new equilibrium in which a larger percentage of ammonia is present.

Changing an equilibrium to a completed reaction. If we were to withdraw the ammonia as fast as it is formed, before it has time to decompose, the reaction ought to go on until either the hydrogen or the nitrogen is used up. The ammonia can be so withdrawn by inclosing the gases over water containing acid during the discharge, and in this case the reaction goes on until one or the other reacting gases is used up. The point of equilibrium can therefore be altered or the equilibrium changed into a completed reaction, by changing the relative masses of the substances taking part in the reaction.

Equilibrium in solution. In aqueous solution we are interested chiefly in the equilibrium of ions. The molecules of an electrolyte keep dissociating into ions, while the ions, on meeting, recombine to form molecules, the result being an equilibrium between the two conditions. Thus, with nitric acid we have the equilibrium

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

If we mix two electrolytes, the equilibrium that is reached is a much more complicated one, for any positive ion may unite with any negative one. At equilibrium all possible ions and combinations of ions will be present. Thus, when we mix sodium nitrate and sulfuric acid in the preparation of nitric acid, we have present the ions Na^+, NO_3^-, H^+, and SO_4^{--}, together with the molecules $NaNO_3$, Na_2SO_4, $NaHSO_4$, HNO_3, and H_2SO_4.

Completion of reactions in solution. The chemist makes use of reactions to secure various compounds in pure condition, and he wishes the yield to be as large as possible. Reactions which stop short of completion and end in an equilibrium are not suited to manufacturing purposes unless means can be found to break up the condition of equilibrium and bring the reaction to a definite conclusion. There are, in general, three conditions under which this may be accomplished.

FIG. 90. The precipitation of silver chloride

1. *A volatile gas may be formed.* If the reaction is conducted under conditions such that one of the products is a gas *insoluble in the solvent*, the gas will make its escape as fast as it is formed. The reaction will then continue until one or the other of the ions taking part in the formation of the gaseous molecules is used up.

For example, when we mix sulfuric acid and sodium nitrate, no visible reaction takes place. But if we heat the mixture above the boiling point of nitric acid, all of this substance formed in the equilibrium between the two ions H^+ and NO_3^- is converted into a gas, insoluble in sulfuric acid. The nitric acid distills away until all of the NO_3^- ions are used up. We then have a completed reaction expressed in the equation

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

2. ***An insoluble solid may be formed.*** When hydrogen chloride (HCl) and silver nitrate ($AgNO_3$) are brought together in solution, we have the two kinds of molecules just named, the ions H^+, Cl^-, Ag^+, NO_3^-, and the new combinations HNO_3 and $AgCl$. One of these, namely silver chloride ($AgCl$), is insoluble in water, and as fast as it is formed it separates from the solution as a curdy white *precipitate* (Fig. 90). The reaction therefore continues until either the ion Ag^+ or the ion Cl^- is used up, the completed equation being

$$(H^+ + Cl^-) + (Ag^+ + NO_3^-) \longrightarrow H^+ + NO_3^- + AgCl$$

3. ***Two different ions may unite to form an undissociated molecule.*** When we bring together in solution sodium hydroxide and hydrochloric acid, we have the ions H^+, Cl^-, Na^+, and OH^-. The H^+ ions and the OH^- ions unite to form molecules of water *which do not again part into ions* save to a very slight extent. This leaves only the ions of $NaCl$ in solution, the equation being

$$(Na^+ + OH^-) + (H^+ + Cl^-) \longrightarrow H_2O + Na^+ + Cl^-$$

Neutralization is practically a completed reaction *because water is so little ionized.*

The preparation of acids. The principle explained in (1) is very frequently applied in the preparation of various acids. Most of the substances that form acids in solution have rather low boiling points, while concentrated sulfuric acid has a rather high boiling point (338°). Consequently, if we take a salt of almost any common acid — a nitrate, a chloride, or an acetate — and treat it with concentrated sulfuric acid, at the same time heating the solution, the volatile acid will boil out of the mixture and can be condensed by cooling the vapor as in the preparation of nitric acid.

Hydrolysis. While water is very little ionized, nevertheless it forms *some* ions. Moreover, when a salt is dissolved in water to form a dilute solution, the relative mass of the water is very great. The reaction of neutralization is therefore reversed to a *slight extent*, forming a small amount of free base and of free acid, thus:

$$NaNO_2 + H_2O \rightleftarrows NaOH + HNO_2$$

A reaction of this kind, in which water acts upon a salt to form a base and an acid, is called *hydrolysis*. If the base formed in hydrolysis is very weak and the acid is strong, the solution will turn blue litmus red, as is true with the salts of aluminium. If the base is very strong and the acid weak, the solution will turn red litmus blue, as is the case with many salts of sodium. If both the acid and the base formed are weak, then the compound may be *completely* hydrolyzed.

EXERCISES

1. Can you mention any reversible reactions, other than those given in this chapter?

2. Suggest a method for the preparation of hydrogen chloride.

3. Would silver nitrate produce a precipitate when added to a solution of sodium chloride (common salt)? If so, how would the precipitate compare in composition with that produced when silver nitrate is added to hydrochloric acid?

4. Barium sulfate ($BaSO_4$) is a white insoluble compound much used as a pigment in making paints. Suggest a method for preparing it.

5. Is the reaction $NH_3 + H_2O \longrightarrow NH_4OH$ reversible? If so, state the conditions under which it will go in each direction.

6. Is the reaction expressed by the equation $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ reversible? If so, state the conditions under which it will go in each direction.

7. Carbonic acid is a very weak acid, while sodium hydroxide is a strong base. How will a solution of sodium carbonate act towards litmus paper?

8. (*a*) In an experiment 10 g. of iron filings and 8 g. of sulfur were mixed and heated until reaction started. What weight of iron sulfide was formed in the reaction? (*b*) In a second experiment 10 g. of iron and 16 g. of sulfur were heated in a similar way. What weight of iron sulfide was formed? (*c*) What difference would you expect to find in the two experiments?

9. In the preparation of hydrogen chloride from sodium chloride and sulfuric acid, why does the reaction go to practical completion?

CHAPTER XX

SULFUR; SELENIUM; TELLURIUM

History and occurrence. Sulfur occupied a prominent place among the few elements known to the ancients, and played an important part in the older views concerning the composition of matter. It occurs in nature in both the free and the combined condition.

In certain volcanic regions, especially in Sicily, large deposits of free sulfur are found, which until recent times constituted the principal source of the world's supply of this element. Free sulfur also occurs in Japan, Spain, Iceland, Mexico, and in different localities in the United States, especially in Louisiana. In combination, sulfur occurs abundantly in the form of sulfides and sulfates. In smaller amounts it is found in a great variety of minerals and is a constituent of many vegetable and animal substances, especially of the yolk of eggs.

FIG. 91. Forcing liquid sulfur from deep wells in Louisiana by means of compressed air

Extraction of sulfur. In Louisiana the sulfur occurs in deposits far underground and covered with quicksand so that it cannot be mined. One of these deposits lies at a depth of 700 feet, is circular in shape, and is about half a mile in diameter and 500 feet in thickness. Wells are drilled into the deposit, and superheated water is forced down through suitable pipes. The hot water melts the sulfur, which is then forced up a separate pipe by compressed air (*A*, Fig. 91). The liquid sulfur then solidifies in very large blocks. A single well has produced 500 tons daily, and the product is 99.5 per cent pure. About 250,000 tons are produced annually from this deposit.

In Sicily a very simple but wasteful method is used to separate sulfur from the rock and earthy materials with which it is mixed. The material is piled up in heaps and set on fire, and the heat from the burning of a part of the sulfur melts another portion, which collects as a liquid at the bottom of the pile. This is drained off and purified by distillation in a retort (*A*) (Fig. 92), the exit tube of which opens into a cooling chamber (*B*) of brickwork. When the sulfur vapor first enters the cold chamber it condenses as a fine crystalline powder called *flowers of sulfur*. As the condensing chamber becomes warm the sulfur condenses as a liquid and is drawn off into cylindrical molds, the product being called *roll sulfur*, or *brimstone*.

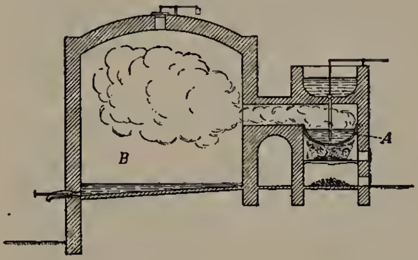


Fig. 92. A sulfur still

Properties. Sulfur is a pale yellow solid without marked taste and with but a faint odor. It is insoluble in water. It melts when heated, forming a thin, straw-colored liquid.

If the temperature is gradually raised, this liquid turns darker in color and becomes thicker until, at about 235°, it is almost black and is so viscous that a vessel containing it can be inverted without danger of the liquid's flowing out. At higher temperatures it becomes mobile again, and at 444.6° boils, forming a yellowish vapor. When the hot sulfur is cooled the same changes take place in reverse order.

Varieties of sulfur. Sulfur exists in a number of allotropic forms (p. 112), which are easy to obtain. The best-known are the following:

1. ***Ordinary, or rhombic, sulfur.*** When sulfur crystallizes from solution in liquids (notably from carbon disulfide) it is obtained in compact yellow crystals which melt at 112.8° and have a density of 2.06. These crystals usually have 8 sides, belong to the rhombic system, and are known as *rhombic sulfur.* Sulfur is often found in a crystalline state in nature (Fig. 93), and these crystals always belong to the rhombic system (see Appendix). Brimstone is composed largely of rhombic sulfur.

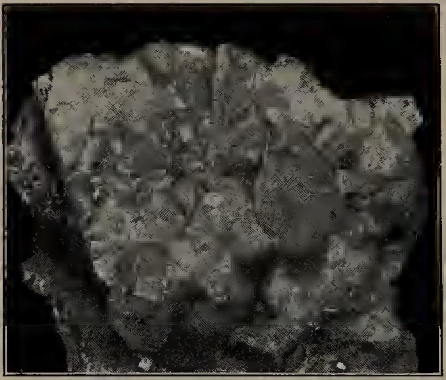


FIG. 93. Crystals of rhombic sulfur as they are found in nature

2. ***Prismatic, or monoclinic, sulfur.*** When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the vessel is in the form of fine needle-shaped crystals, which melt at 119.2° and have a density of 1.96. The needle-shaped form is called *monoclinic sulfur*, since the crystals belong to the monoclinic system.

Relation of rhombic to monoclinic sulfur. Experiments have shown that whenever sulfur crystallizes at ordinary temperature the rhombic form is obtained; when crystallized at higher temperatures, as when the sulfur is melted and allowed to cool, the monoclinic form is obtained. Moreover, the temperature below which sulfur assumes the rhombic form and above which it assumes the monoclinic form is a perfectly definite one; namely, 95.5°. At this temperature, known as the *transition temperature*, the two forms of crystals remain unchanged when in contact with each other. If heated above 95.5°, the rhombic form gradually changes into the monoclinic form; if cooled below 95.5°, the monoclinic gradually changes into the rhombic form. This change of one form into the other ordinarily takes place very slowly, so that some days may be required before the change is complete. It has also been found that an increase of pressure promotes the change from rhombic sulfur into monoclinic sulfur.

Amorphous sulfur. In discussing the physical properties of sulfur, attention was called to the fact that sulfur is easily melted and forms a pale-yellow, mobile liquid, which at a higher temperature becomes dark and viscous. At intermediate temperatures the liquid obtained consists of varying amounts of the mobile liquid ($S\lambda$) and the viscous liquid ($S\mu$) in equilibrium with each other. If the molten sulfur is heated to boiling and poured into cold water, the sudden chilling prevents the crystallization of the viscous liquid, so that an amorphous, dough-like product is obtained. This form is insoluble in carbon disulfide and is known as plastic sulfur. It is simply a mixture of the two liquid forms in a very much undercooled state (p. 109). On standing, plastic sulfur changes in part into rhombic crystals.

The formation of plastic sulfur is shown in a very striking manner by distilling sulfur from a small, short-necked retort (Fig. 94) and allowing the distillate to run into cold water.

Chemical conduct of sulfur. When sulfur is heated to ignition in oxygen or in the air, it burns with a pale-blue flame and forms sulfur dioxide (SO_2). Small quantities of sulfur trioxide (SO_3) may also be formed in the combustion of sulfur. Most metals when heated with sulfur combine directly with it, forming metallic sulfides. In some cases the action is so energetic that the mass becomes incandescent, as has been seen in the case of iron uniting with sulfur. This property recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine quite readily with sulfur.

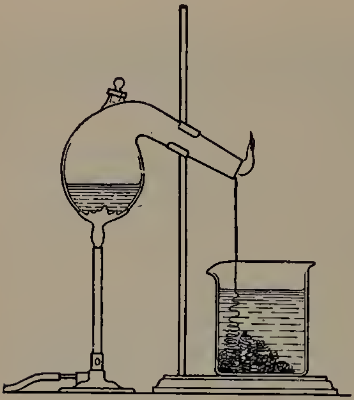


FIG. 94. The preparation of plastic sulfur

Uses of sulfur. Large quantities of sulfur are used in the manufacture of gunpowder, vulcanized rubber, carbon disulfide, sulfur dioxide, sulfuric acid, and salts of various kinds. It is also used extensively in the manufacture of insecticides for use in orchards and vineyards.

Lime-sulfur spray. The chief sulfur insecticide is known as *lime-sulfur spray.* It is made by boiling sulfur with slaked lime, by which process a deep-red liquor is obtained which consists essentially of a solution of sulfides of calcium (CaS_4 and CaS_5). The liquid is a very efficient insecticide, particularly for scale, and it is also a fungicide. Large quantities of it are used for spraying fruit trees.

COMPOUNDS OF SULFUR WITH HYDROGEN

The following compounds of sulfur with hydrogen are known: hydrogen sulfide (H_2S), a foul-smelling gas; hydrogen persulfide, a liquid which is probably a mixture of the sulfides H_2S_4 and H_2S_5.

Hydrogen sulfide (H_2S). Hydrogen sulfide is present in the vapors issuing from volcanoes. Dissolved in water, it constitutes the so-called sulfur waters of common occurrence. It is formed when organic matter containing sulfur undergoes decay, and the disagreeable odor attending such changes is due in part to the presence of this gas.

Preparation. Hydrogen sulfide is prepared in the laboratory by treating a sulfide with an acid. Iron sulfide (FeS) and hydrochloric acid are usually employed:

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S$$

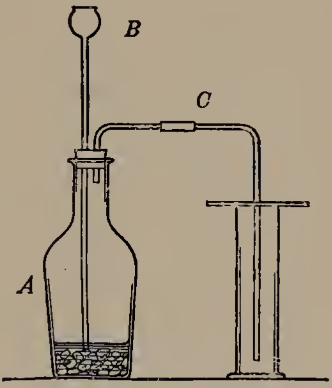


FIG. 95. The preparation of hydrogen sulfide

A convenient apparatus is shown in Fig. 95. A few lumps of iron sulfide are placed in the bottle *A*, and dilute acid is added a little at a time through the funnel tube *B*. The gas escapes through the tube *C* and may be collected by displacement of air; or it may be passed into water, forming a solution. The Kipp generator (Fig. 17) is more convenient than the above apparatus if a larger quantity of the gas is desired.

Properties. Hydrogen sulfide is a colorless gas having a mild, disagreeable taste and an offensive odor. It is 1.18 times as heavy as air. When liquefied it boils at – 61.6° and freezes at – 82°. One volume of water at 15°

dissolves 3.05 volumes of the gas. When this solution is heated to boiling, the gas is all expelled. In pure form it acts as a violent poison and, even when diluted largely with air, produces headache, dizziness, and nausea. Fortunately its extremely disagreeable odor gives warning of its presence.

Chemical conduct. 1. ***Acid properties.*** In aqueous solution hydrogen sulfide is slightly dissociated, giving hydrogen ions. The solution therefore acts as a weak acid and is known as *hydrosulfuric acid.* It possesses the general properties of an acid, turning blue litmus red and neutralizing bases with the formation of sulfides.

2. ***Action of heat.*** When heated to a high temperature hydrogen sulfide is decomposed into its elements, the speed of decomposition being marked at 500°.

3. ***Action of oxygen.*** When a solution of hydrogen sulfide in water is exposed to the air, the hydrogen of the sulfide unites with oxygen to form water, while the sulfur is liberated and settles to the bottom of the liquid. In this way are formed the deposits of sulfur found about many springs. At a high temperature hydrogen sulfide burns readily in either oxygen or air according to the equation

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When there is not sufficient oxygen to combine with both the sulfur and the hydrogen, the latter element combines with the oxygen and the sulfur is set free:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

4. ***Reducing action.*** Because of the hydrogen present, together with the ease with which it is given up in contact with an oxidizing agent, hydrogen sulfide acts as a strong reducing agent. Thus, when it is bubbled through

concentrated nitric or sulfuric acid, both of which are strong oxidizing agents, the hydrogen of the sulfide combines with a portion of the oxygen of the acid to form water, the acid being at the same time reduced.

A much-used method of drying gases consists in bubbling them through concentrated sulfuric acid, which absorbs the moisture. It is evident, however, from the statements just made, that this method cannot be used for drying hydrogen sulfide.

5. *Action on metals.* Hydrogen sulfide acts upon many metals, forming *sulfides.* Silver sulfide (Ag_2S) is black, and it is owing to traces of hydrogen sulfide in the air that silver objects tarnish.

Salts of hydrosulfuric acid; sulfides. The salts of hydrosulfuric acid, or sulfides, form an important class of compounds, and many occur in nature. They are all solids; most of them are insoluble in water, while some are insoluble even in acids. As prepared in the laboratory, some of these salts, such as copper sulfide (CuS) and silver sulfide (Ag_2S), are black; others, as cadmium sulfide (CdS) and arsenic sulfide (As_2S_3), are yellow; while zinc sulfide (ZnS) is white.

The soluble sulfides, Na_2S, K_2S, $(NH_4)_2S$, are most readily prepared by treating the appropriate base with hydrosulfuric acid; the insoluble sulfides may be prepared by heating the metals with sulfur, although the general and more convenient method for their preparation consists in passing hydrogen sulfide into the aqueous solutions of appropriate salts of the metals. Thus, copper sulfide may be prepared by dissolving copper sulfate ($CuSO_4$) in water and passing hydrogen sulfide into the solution:

$$H_2S + CuSO_4 \longrightarrow CuS + H_2SO_4$$

The copper sulfide, being insoluble, precipitates as fast as formed, and may be removed from the liquid by filtration.

The preparation of these sulfides as carried out in the laboratory may be illustrated in the following way: Hydrogen sulfide is generated in a Kipp apparatus *A* (Fig. 96) and is passed successively into bottles *B*, *C*, *D*, and *E*, containing, respectively, the aqueous solutions of silver nitrate, cadmium sulfate, zinc acetate, and sodium hydroxide. As the gas bubbles through the solutions there is formed black silver sulfide (Ag_2S) in *B*, yellow cadmium sulfide (CdS) in *C*, white zinc sulfide (ZnS) in *D*. No precipitate is produced in *E*, for although sodium sulfide is formed, it is soluble in water and therefore does not separate.

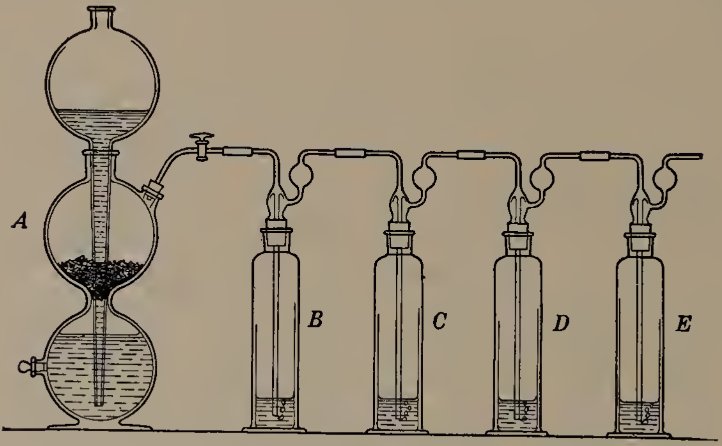


FIG. 96. The preparation of insoluble sulfides by precipitation with hydrogen sulfide

Oxides of sulfur. Sulfur forms five different oxides. The two most important are sulfur dioxide (SO_2) and sulfur trioxide (SO_3). Both are acid anhydrides.

Sulfur dioxide (sulfurous anhydride) (SO_2). This is the well-known gas resulting from the combustion of sulfur. It occurs in nature in the gas issuing from volcanoes and in solution in the waters of some springs.

Preparation. Sulfur dioxide is prepared by three general methods:

1. *By the combustion of sulfur or a metallic sulfide.* In either case the sulfur is converted into sulfur dioxide:

$$S + O_2 \longrightarrow SO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

The enormous quantities of sulfur dioxide used in the manufacture of sulfuric acid are prepared by this general method.

2. *By the reduction of sulfuric acid.* When concentrated sulfuric acid is heated with certain metals, such as copper, a part of the acid is reduced to sulfurous acid. The latter compound then decomposes into sulfur dioxide and water, the complete equation being as follows:

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\,H_2O$$

3. *By the action of acids upon a sulfite.* Sulfites are salts of sulfurous acid (H_2SO_3). When an acid, such as hydrochloric acid, is added to a sulfite, sulfurous acid is formed, which decomposes into water and sulfur dioxide. The reactions are expressed in the following equations:

$$Na_2SO_3 + 2\,HCl \rightleftarrows 2\,NaCl + H_2SO_3 \qquad (1)$$
$$H_2SO_3 \rightleftarrows H_2O + SO_2 \qquad (2)$$

Explanation of the reaction. In the action of hydrochloric acid upon sodium sulfite, as expressed in these equations, we have two reversible reactions depending upon each other. It might be expected that the reaction expressed in equation (1) would result in an equilibrium, since none of the substances represented in the equation are insoluble or volatile in the presence of water. The sulfurous acid, however, decomposes as fast as it forms, according to equation (2), the resulting sulfur dioxide escaping in the form of a gas.

The reaction continues, therefore, until practically all the sodium sulfite has been decomposed. Since sulfur dioxide is quite soluble in water, it is evident that the reaction should be carried out in the presence of as little water as possible; otherwise a proportionately larger quantity of sulfur dioxide will remain in solution, and the reaction will not reach the same degree of completion.

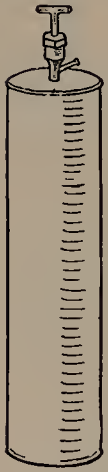


Fig. 97. Cylinder of liquefied sulfur dioxide

Properties. Sulfur dioxide is a colorless gas which at ordinary temperatures is 2.2 times as heavy as air. It has a peculiar, irritating odor. The gas is very soluble in water, 1 volume of water dissolving approximately 80 volumes of the gas under standard conditions. It is easily condensed to a colorless liquid (boiling point, – 8°) and can be purchased in this condition, stored in strong bottles or in tin cylinders (Fig. 97).

Chemical conduct. Sulfur dioxide has a marked tendency to combine with other substances and is therefore an active substance chemically. It has a marked affinity for oxygen and is therefore a reducing agent. Under some conditions it can also act as an oxidizing agent. Thus, it reacts with hydrogen sulfide to form water and sulfur, as follows:

$$2\,H_2S + SO_2 \longrightarrow 2\,H_2O + 3\,S$$

Since both hydrogen sulfide and sulfur dioxide are present in the gases issuing from volcanoes, it is probable that the large deposits of sulfur occurring in volcanic regions have resulted from the interaction of these two gases, according to the above equation. A characteristic property of sulfur dioxide is its conduct towards water, with which it combines to form sulfurous acid.

Sulfurous acid (H_2SO_3). When sulfur dioxide is passed into water some of the gas combines with water to form sulfurous acid (H_2SO_3), while the remainder is held in a state of solution. The sulfurous acid formed is in equilibrium, on the one hand, with water and dissolved sulfur dioxide and, on the other hand, with the ions H^+ and HSO_3^-, resulting from the ionization of a portion of the acid:

$$H_2O + SO_2 \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$

When heated this liquid acts as if it were simply a solution of sulfur dioxide in water, all the sulfur being evolved as sulfur dioxide. Toward a base, on the other hand, it acts simply as a solution of sulfurous acid (compare with aqua ammonia, p. 204).

Because of its unstable character sulfurous acid can be obtained only in the form of a dilute solution. This solution has the following properties:

1. ***Acid properties.*** The solution has all the properties typical of a very weak acid. When neutralized by bases sulfurous acid yields a series of salts called *sulfites*, most of which are insoluble in water.

2. ***Reducing properties.*** Solutions of sulfurous acid act as good reducing agents. This is due to the fact that sulfurous acid has the power of taking up oxygen from the air or from substances rich in oxygen, and is changed by this reaction into sulfuric acid:

$$2\,H_2SO_3 + O_2 \longrightarrow 2\,H_2SO_4$$

3. ***Bleaching properties.*** Sulfurous acid has strong bleaching properties. It is on this account used to bleach paper, straw goods, and even such foods as canned corn and dried fruits. As a rule the bleaching is not permanent. It is not so efficient a bleaching agent as chlorine, and for

this reason is used in bleaching only such materials as are injured by the action of chlorine.

The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 98) in which has been placed a highly colored flower moistened with water. Straw hats may be cleaned and brightened in a similar way.

4. ***Antiseptic properties.*** Sulfurous acid has marked antiseptic properties, and on this account has the power of arresting fermentation. It is therefore used in certain foods containing sugars, such as sweet cider, canned corn, and dried fruits. Whether or not its use in foods should be permitted is a much debated question.

FIG. 98. Bleaching a flower with sulfur dioxide

Salts of sulfurous acid; sulfites. Since it contains two hydrogen atoms, sulfurous acid forms both acid and normal salts. Thus, with sodium it forms the salts $NaHSO_3$ and Na_2SO_3. The sulfites are all solid substances and, like sulfurous acid itself, combine readily with oxygen, forming the corresponding sulfates. They are therefore good reducing agents. Because of this property, unless freshly prepared, they are apt to contain more or less of the corresponding sulfates. Calcium acid sulfite is used in the manufacture of paper from wood, since it dissolves the objectionable constituent (lignin) of the wood, leaving the pure cellulose, which is the material desired for the manufacture of paper.

Sulfur trioxide (sulfuric anhydride) (SO_3). When sulfur is burned in oxygen minute quantities of sulfur trioxide are formed along with the sulfur dioxide. Likewise, when sulfur dioxide and oxygen are heated together, combination takes place, but the speed of the reaction is so slow that only traces of the trioxide result. In the presence of a catalytic agent, however, such as finely divided platinum, the speed is greatly increased, and in this way sulfur trioxide can be obtained in quantities. The reaction is a reversible one, as is shown in the following equation:

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3 + 2 \times 22{,}600 \text{ cal.}$$

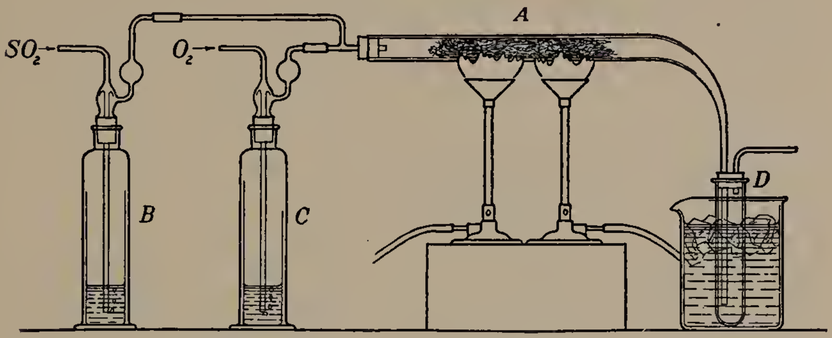


FIG. 99. The preparation of solid sulfur trioxide

The largest yield of sulfur trioxide is obtained when the reaction is carried out at approximately 400°, at which temperature about 98 per cent of the sulfur dioxide combines with oxygen.

The preparation of the trioxide by the last-named method can be carried out in the laboratory as follows: The platinum used as a catalytic agent is prepared by moistening asbestos fiber in a solution of chloroplatinic acid and igniting it in a flame, whereby the platinum compound is reduced to metallic platinum. The fiber containing the finely divided platinum is placed in a tube of hard glass *A* (Fig. 99), which is then heated to about 400°, while equal volumes of sulfur dioxide and oxygen, previously dried by bubbling them through sulfuric acid (contained in bottles *B* and *C*), are passed into the tube.

As this mixture comes in contact with the catalytic agent combination takes place, and the resulting sulfur trioxide escapes from the jet at the end of the tube and may be condensed by surrounding the receiving tube *D* with a freezing mixture.

Properties of sulfur trioxide. Sulfur trioxide is a colorless liquid which solidifies at about 15° and boils at 46°. A trace of moisture causes it to solidify into a mass of silky white crystals somewhat resembling asbestos fiber in appearance. These crystals have the formula $(SO_3)_2$, or S_2O_6. In contact with the air sulfur trioxide fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulfuric acid, so that sulfur trioxide is the *anhydride* of that acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Sulfuric acid (H_2SO_4). Sulfuric acid has long been known, and was one of the most important reagents employed by the alchemists. It is by far the most largely used of all the acids. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are consumed in the industries, especially in the manufacture of fertilizers, the refining of petroleum, and in cleaning scale from iron and steel.

Manufacture of sulfuric acid. Two general methods for the manufacture of sulfuric acid are in use at the present time. These are known as the contact process and the lead-chamber process.

1. ***Contact process.*** The reactions taking place in this process are represented by the following equations:

$$S + O_2 \longrightarrow SO_2 \qquad (1)$$

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3 \qquad (2)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (3)$$

Sulfur dioxide is prepared according to equation (1), by burning sulfur or some sulfide, such as iron pyrite (FeS_2), in air. The resulting sulfur dioxide, together with sufficient air to furnish the necessary oxygen, is conducted through iron tubes filled with some porous material (asbestos or sodium sulfate), through which a suitable catalytic agent, such as platinum or iron oxide, is interspersed, the material being kept at about 400°. Under these conditions sulfur trioxide is formed according to equation (2). The resulting sulfur trioxide is then brought into contact with water, with which it unites to form sulfuric acid according to equation (3).

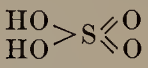
The only part of the process which is difficult to carry out on a commercial scale is the formation of the sulfur trioxide. It has long been known that sulfur dioxide and oxygen combine when passed over finely divided platinum, but the cost of platinum, together with the poor yield of sulfur trioxide obtained, made the process an impracticable one. A study of the conditions under which the reaction takes place resulted in improvements in the process, until finally, in 1901, the German chemist Knietsch succeeded in overcoming the difficulties to such an extent as to make the process a commercial success for the manufacture of the pure, concentrated acid. While platinum is the most effective catalytic agent for the process, it is very expensive, its commercial value at the present time being greater than that of gold. This has led to the use of other catalytic agents, among which iron oxide appears to be the best.

It is an interesting fact that the sulfur trioxide produced by this method will not combine with pure water. It is conducted into concentrated sulfuric acid and combines readily with the water present in this reagent.

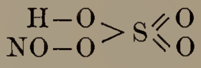
2. *Chamber process.* The older method of manufacture, exclusively employed until recent years and still the most important process, is much more complicated. The conversion

of water, sulfur dioxide, and oxygen into sulfuric acid is accomplished by the catalytic action of oxides of nitrogen. Since these oxides are gases, it is difficult to prevent their escape, and very elaborate precautions have to be taken to reduce the loss as much as possible. The reactions are brought about in large, lead-lined chambers, into which oxides of nitrogen, sulfur dioxide, steam, and air are introduced in suitable proportions. These react to form sulfuric acid, which collects on the floor of the chambers and is drawn off from time to time.

Reactions of the chamber process. The reactions involved are quite complex, and are not at all thoroughly understood. It is believed, however, that the two following general reactions take place: (1) The substances introduced into the chambers first react to form a derivative of sulfuric acid known as nitrosyl sulfuric acid. The relation of these two compounds to each other may be seen from their structural formulas:

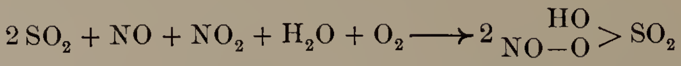


sulfuric acid



nitrosyl sulfuric acid

The reaction may be represented as follows:



$$2\,SO_2 + NO + NO_2 + H_2O + O_2 \longrightarrow 2\,\begin{matrix}HO\\NO-O\end{matrix}\!>SO_2 \qquad (1)$$

This acid can be obtained in the form of white crystals known as *chamber crystals.*

(2) In the commercial manufacture of sulfuric acid, however, such a separation does not occur, because sufficient water is always present to change the nitrosyl acid, as fast as formed, into sulfuric acid:

$$2\,\begin{matrix}HO\\NO-O\end{matrix}\!>SO_2 + H_2O \longrightarrow 2\,H_2SO_4 + NO + NO_2 \qquad (2)$$

It will be noted that in equation (2) the same quantities of the oxides of nitrogen are formed as are required for equation (1). Theoretically, therefore, a small amount of these oxides should suffice to prepare an unlimited amount of sulfuric acid; practically, some of the oxides are lost, and this loss must be replaced.

The sulfuric acid plant. The simpler parts of a plant used in the manufacture of sulfuric acid are illustrated in Fig. 100. Sulfur or some sulfide, as FeS_2, is burned in the furnace *A*. The resulting sulfur dioxide, together with the necessary amount of air, passes into the structure *C*, known as the Glover tower. In it the oxides of nitrogen are generated, as will be explained later, and these, together with the sulfur dioxide and air, pass into the chambers *D*, *D*. Water or steam is also introduced into these chambers at suitable points. Here the reactions take place which result in the formation of the sulfuric acid. The nitrogen remaining after the withdrawal of the oxygen from the air which entered the chamber escapes through the structure *E*, known as the Gay-Lussac tower. In order to prevent the escape of the nitrogen dioxide regenerated in the reaction, this tower is filled with pieces of coke over which trickles concentrated sulfuric acid admitted in the form of a spray (*F*) at the top. The concentrated acid absorbs the nitrogen dioxide but not the nitric oxide, so that the latter escapes along with the nitrogen. The acid which is sprayed into the top of the tower collects in the bottom and is run off into the vessel *G*, from which it is forced into the tank at the top of the Glover tower *C*. Here it is mixed with some dilute

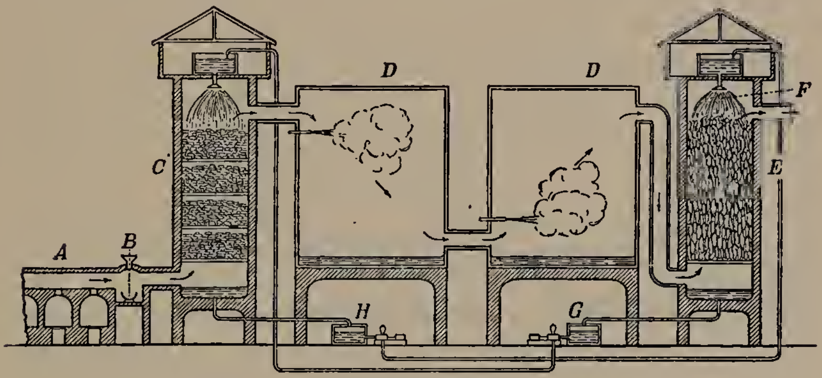


Fig. 100. Diagram of a plant for the manufacture of sulfuric acid

sulfuric acid, and the mixture sprayed into the top of the tower, which is partly filled with some acid-resisting rock. As the acid passes down through this material it meets with the hot gases entering from the furnace, whereby the nitrogen dioxide is liberated from the acid, passes over into the chambers *D*, *D*, and again enters into the reaction. During the process just described the dilute acid becomes sufficiently concentrated to serve again as an absorbent of nitrogen dioxide. The necessary quantity of it is therefore run into the vessel *H* from the bottom of the tower, and then forced into the tank at the top of *E*. In order to replace the oxides of nitrogen lost in the process, the necessary quantity is added by the action of sulfuric acid upon sodium nitrate in vessel *B*. The sulfuric acid so formed, together with the excess of condensed steam, collects upon the floor of the chambers in the form of a liquid containing from 62 to 70 per cent of hydrogen sulfate. The product is called *chamber acid* and is quite impure; but for many purposes, such as the manufacture of fertilizers, it needs no further treatment. It can be concentrated by evaporation in vessels variously made of iron, platinum, or silica.

Relative advantages of the contact process and the lead-chamber process. It will be noted that in the contact process it is just as easy to prepare the pure concentrated acid as the dilute acid. In the chamber process, however, the dilute acid is obtained first and can be prepared at a very low cost. The concentration and purification of the dilute acid is, however, an expensive operation. For these reasons the contact process can compete with the lead-chamber process only in the manufacture of the pure concentrated acid.

Properties. Pure anhydrous sulfuric acid, more properly named *hydrogen sulfate*, is a colorless, oily liquid nearly twice as heavy as water. The ordinary concentrated acid contains about 2 per cent of water, has a density of 1.84, and boils at 338°. It is sometimes called *oil of vitriol*, since it was formerly made by distilling a mixture of substances, one of which was called *green vitriol*.

Chemical conduct. Sulfuric acid possesses chemical properties which make it one of the most important of chemical substances.

1. ***Acid properties.*** In concentrated aqueous solutions, hydrogen sulfate forms the ions H^+ and HSO_4^-, the latter, on further dilution of the solution, breaking down into the ions H^+ and SO_4^{--}. It is this aqueous solution containing hydrogen ions which is properly termed sulfuric acid.

2. ***Action as an oxidizing agent.*** Sulfuric acid contains a large percentage of oxygen and is, like nitric acid, a very good oxidizing agent. When the concentrated acid is heated with sulfur or carbon or various other substances, oxidation takes place, the sulfuric acid decomposing according to the equation

$$H_2SO_4 \longrightarrow H_2SO_3 + [O]$$

3. ***Action on metals.*** A *dilute solution* of sulfuric acid acts upon the metals that precede hydrogen in the electrochemical series (p. 191), forming a sulfate of the metal and hydrogen. Such a solution has no action upon the metals that follow hydrogen in the series.

On the other hand, the *concentrated* acid acts upon a number of the metals without respect to their position in the electrochemical series; but in all these cases the first action is one of oxidation. With copper the reaction is represented by the equation

$$Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2$$

The copper oxide then dissolves in an additional quantity of sulfuric acid to form copper sulfate:

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

These two equations can be combined into the form

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2$$

4. ***Action on salts.*** We have repeatedly seen that an acid of high boiling point, heated with the salt of some acid of lower boiling point, will drive out the low-boiling acid (p. 225). The boiling point of sulfuric acid (338°) *is higher than that of almost any common acid*; hence it is largely used in the preparation of other acids.

5. ***Action on water.*** Concentrated sulfuric acid has a very great affinity for water, and when mixed with water much heat is evolved. It is therefore an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by bubbling them through the concentrated acid.

Not only can sulfuric acid absorb water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even animal tissues, all of which contain much oxygen and hydrogen in addition to carbon, are charred by the action of the concentrated acid. The process in general consists in the withdrawal of the oxygen and hydrogen present in the compound, thus leaving the black carbon as a residue.

Salts of sulfuric acid; sulfates. The sulfates constitute a very important class of compounds, and many of them have extensive commercial uses. The normal salts are all solids and, with the exception of those of barium, strontium, and lead, are soluble in water. Several others, notably calcium sulfate and silver sulfate, are only slightly soluble.

Other oxygen acids of sulfur. In addition to sulfurous and sulfuric acids a number of other oxygen acids of sulfur are known, either in the free state or in the form of their salts. The following are the most important:

1. ***Pyrosulfuric acid*** **($H_2S_2O_7$).** This is a solid crystalline compound prepared by the union of sulfuric acid and sulfur trioxide:

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

The acid and its salts are strong oxidizing agents. The fuming sulfuric acid of commerce consists of a mixture of sulfuric and pyrosulfuric acids.

2. ***Persulfuric acid*** **($H_2S_2O_8$).** This acid is unstable and exists only in dilute solution. Its salts, however, are stable. They are prepared by the electrolysis of concentrated solutions of the corresponding acid sulfates. Thus, $KHSO_4$ by electrolysis yields $K_2S_2O_8$. The salts of persulfuric acid are very strong oxidizing agents. Thus, ammonium persulfate, $(NH_4)_2S_2O_8$, is often used as an oxidizing agent, especially in connection with certain photographic processes.

Monobasic and dibasic acids. Such acids as hydrochloric and nitric acids, whose molecules have only one replaceable hydrogen atom, or, in other words, yield one hydrogen ion in solution, are called *monobasic* acids. Acids whose molecules yield two hydrogen ions in solution are called *dibasic* acids. Similarly, we may have *tribasic* and *tetrabasic* acids. The three acids of sulfur are dibasic acids. It is therefore possible for each of them to form both normal and acid salts.

Preparation of acid salts. The acid salts can be made in two ways: the acid may be treated with only half enough base to neutralize it, —

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$

or a normal salt may be treated with the free acid, —

$$Na_2SO_4 + H_2SO_4 \longrightarrow 2\,NaHSO_4$$

Carbon disulfide (CS_2). When sulfur vapor is passed over highly heated carbon, the two elements combine, forming carbon disulfide:

$$C + 2\,S \longrightarrow CS_2 - 19{,}600 \text{ cal.}$$

Since heat is *absorbed* in this reaction, it must be supplied from external sources, and the reaction will proceed only at a rather high temperature.

Carbon disulfide is a heavy, colorless, highly refractive liquid which boils at 46°. When pure it has a pleasant odor, but it gradually undergoes slight decomposition and acquires a most disagreeable odor. Its vapor is very inflammable, burning in the air to form carbon dioxide and sulfur dioxide:

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$$

Carbon disulfide is a good solvent for many substances, such as gums, resins, and waxes, which are not soluble in most liquids, and it is therefore used as a solvent for such substances. It is also used as an insecticide. Its vapor is poisonous as well as highly inflammable, so that one must exercise great care in working with it.

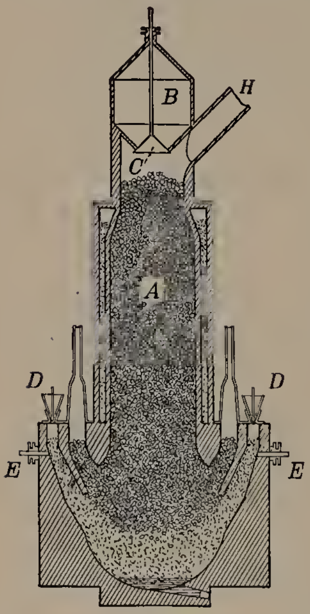


FIG. 101. An electric furnace for the production of carbon disulfide

Commercial preparation of carbon disulfide. Commercially, carbon disulfide is made by the direct combination of carbon and sulfur, the heat necessary for this union being derived from an electric current. The main part of a large furnace *A* (Fig. 101) is filled with charcoal introduced through the trap *C*. Sulfur is added through the hoppers *D*, *D*. An electric current is passed in at *E*, *E*. The heat generated is sufficient to vaporize the sulfur, which then unites with the hot carbon to form carbon disulfide. The vapors escape at *H* and are condensed. Some of the furnaces are 40 ft. in height and yield as much as 25,000 lb. of the disulfide in twenty-four hours.

Selenium and tellurium. These two rather uncommon elements are closely related to sulfur in their chemical conduct. They are usually found associated with sulfur and sulfides, either as the free elements or, more commonly, in combination with metals. With hydrogen they form compounds of the formulas H_2Se and H_2Te; these bodies are gases with properties very similar to those of H_2S. They also form oxides and oxygen acids which resemble the corresponding sulfur compounds. The elements even have forms corresponding very closely to those of sulfur.

The hydrates. Attention has been called to the fact that many compounds combine directly with water, forming new compounds known as *hydrates.* Many salts possess this property in a marked degree, forming hydrated salts. Thus, when copper sulfate ($CuSO_4$) is dissolved in water and the solution is set aside, a crystalline hydrate is deposited which is formed by the union of 1 molecule of copper sulfate with 5 molecules of water, and its formula is written $CuSO_4 \cdot 5\,H_2O$. Commercially, this hydrate is called *blue vitriol.* Similarly, magnesium sulfate ($MgSO_4$) forms the crystalline hydrate $MgSO_4 \cdot 7\,H_2O$. If we wish to distinguish between the salt and its hydrate, the salt is referred to as the *anhydrous* compound. Thus, the salt $CuSO_4$ is termed anhydrous copper sulfate. The hydrates are true chemical compounds, any given hydrate being formed by the union of definite weights of the anhydrous compound and of water. Many anhydrous compounds, however, combine with several different percentages of water to form different hydrates. The hydrates as a rule are not very stable and tend to decompose into the constituents from which they are formed, especially when heated. On the other hand, many anhydrous salts, such as calcium chloride, absorb moisture from the air and form hydrates.

Efflorescence. All hydrates may be regarded as tending to lose water at ordinary temperatures, the reaction being reversible; thus,

$$Na_2SO_4 \cdot 10\,H_2O \rightleftarrows Na_2SO_4 + 10\,H_2O$$

If crystals of a hydrate are placed in a closed space, the reaction goes on until the pressure of the water vapor formed reaches a definite value, and then equilibrium results. If this pressure is greater than the pressure of water vapor in the air, the crystal will lose water when exposed to the air and crumble to powder. Such crystals are said to be *efflorescent.* Hydrated sodium sulfate is a good example of an efflorescent compound.

EXERCISES

1. Is the equation for the preparation of hydrogen sulfide a reversible one? As ordinarily carried out, does the reaction complete itself?

2. Suppose that hydrogen sulfide were a liquid; would it be necessary to modify the method of preparation?

3. Does perfectly dry hydrogen sulfide change the color of litmus paper? State reason for your answer.

4. What is an acid anhydride? Aside from those of sulfur, what other anhydrides have been mentioned?

5. How would you expect dilute sulfuric acid to act upon iron? upon silver? (Refer to electrochemical series.)

6. Can you suggest a reason why silver spoons become tarnished when in contact with certain kinds of food?

7. Mention other instances of catalysis aside from those given in this chapter.

8. In the commercial preparation of carbon disulfide what is the function of the electric current?

9. Write the equation representing the reaction between hydrosulfuric acid and sodium hydroxide; between hydrosulfuric acid and ammonium hydroxide.

10. Show that the preparation of sulfur dioxide from a sulfite is similar in principle to the preparation of hydrogen sulfide.

11. Calculate the weight of materials necessary for the preparation of sufficient hydrogen sulfide to saturate 20 l. of water at 15° and normal pressure.

12. What weight of sulfur is necessary for the preparation of 2000 lb. of sulfuric acid containing 5 per cent of water?

13. Suppose you wish to prepare 100 kg. of blue vitriol; calculate the weights of materials necessary for its preparation.

14. 50 g. of blue vitriol was dissolved in water, and hydrogen sulfide passed through the solution until the copper was all precipitated. Calculate the weight of the precipitate.

15. Write the names and formulas of the oxides and oxygen acids of selenium and tellurium.

16. Contrast the action of dilute sulfuric acid and of concentrated sulfuric acid upon zinc.

17. How many calories of heat are absorbed in the preparation of 10 kg. of carbon disulfide?

18. Write equations for the preparation of sodium acid sulfite by two different methods.

CHAPTER XXI

THE PERIODIC LAW

A number of the elements have now been studied somewhat closely. Of these, oxygen, hydrogen, nitrogen, and chlorine, while having some physical properties in common with each other, have almost no points of similarity in their chemical conduct. On the other hand, oxygen and sulfur, while quite different physically, have much in common in their chemical properties.

More than eighty elements are now known. If all of these should have properties as diverse as do oxygen, hydrogen, nitrogen, and chlorine, the study of chemistry would plainly be very difficult and complicated. If, however, the elements can be classified in groups the members of which have very similar properties, the study will be very much simplified.

Earlier classification of the elements. Even at an early period efforts were made to discover some natural principle in accordance with which the elements could be classified. Two of these classifications may be mentioned here.

1. *Classification into metals and nonmetals.* The classification into metals and nonmetals most naturally suggested itself. This grouping was based largely on physical properties, the metals being heavy, lustrous, malleable, ductile, and good conductors of heat and electricity. Elements possessing these properties are usually base-forming in character, and the ability to form bases came to be regarded as a

characteristic property of the metals. The nonmetals possessed physical properties which were opposite to those of the metals, and were acid-forming in character.

Not much was gained by this classification, and it was very imperfect. Some metals, as potassium, are very light; some nonmetals, as iodine, have a high luster; some elements can form either an acid or a base.

2. ***Classification into triad families.*** In 1825 Döbereiner observed that an interesting relation exists between the atomic weights of chemically similar elements. To illustrate, lithium, sodium, and potassium resemble each other very closely, and the atomic weight of sodium is almost exactly an arithmetical mean between those of the other two: $\frac{6.94 + 39.10}{2} = 23.02$. In many chemical and physical properties sodium is midway between the other two.

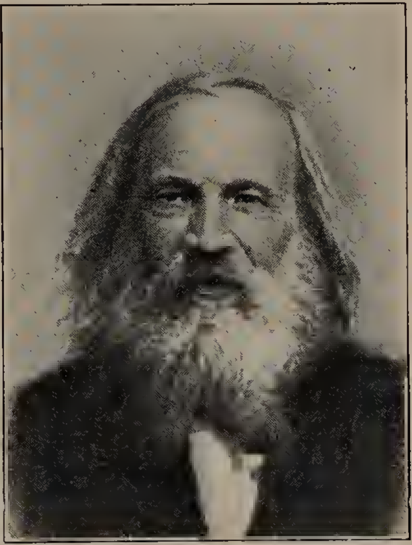


FIG. 102. Mendeléeff (1834–1907)

A Russian chemist who proposed the periodic classification of the elements

A number of triad families were found, but among eighty elements, whose atomic weights range all the way from 1 to 240, such agreements might be mere chance. Moreover, many elements did not appear to belong to such families.

Periodic classification. In 1869 the Russian chemist Mendeléeff (Fig. 102) devised an arrangement of the elements based on their atomic weights which has proved to be of great service in the comparative study of the elements.

A few months later the German, Lothar Meyer, independently suggested the same ideas. This arrangement brought to light a great generalization, now known as the *periodic law.* An exact statement of the law will be given in a later paragraph.

Arrangement of the periodic table. The general arrangement suggested by Mendeléeff and extended so as to include elements more recently discovered is as follows: Omitting hydrogen, which has the smallest atomic weight, and beginning with helium, which has an atomic weight of 3.99, the first eight elements are arranged in a horizontal row in the order of their atomic weights. These eight elements all differ markedly from each other, but the one having the next highest atomic weight, neon, is very similar to helium. It is placed just under helium, and a new horizontal row follows as shown below. The element following chlorine, namely argon, resembles helium and neon and begins a third row. These three rows are as follows:

He (3.99)	Li (6.94)	Gl (9.1)	B (11)	C (12.005)	N (14.01)	O (16)	F (19)
Ne (20.2)	Na (23)	Mg (24.32)	Al (27.1)	Si (28.3)	P (31.04)	S (32.06)	Cl (35.46)
A (39.88)	K (39.1)	Ca (40.07)	Sc (44.1)	Ti (48.1)	V (51)	Cr (52)	Mn (54.93)

If now we consider the elements that fall into vertical columns in these three rows, a remarkable fact is brought to light. Not only is there a strong similarity between helium, neon, and argon, which form the first vertical column, but the elements in the other columns exhibit much of the same kind of similarity among themselves, and evidently form natural groups. Thus lithium, sodium, and potassium resemble each other very closely and form one of Döbereiner's triads.

Iron, cobalt, and nickel, following manganese (Mn), have atomic weights near together, and are very similar chemically. They do not strongly resemble any of the elements so far considered, and so are placed in a group by themselves. The first three horizontal rows of the table on the next page show the arrangement of these twenty-seven elements. A new horizontal row is begun with copper. Following the fifth and seventh rows are groups of three closely related elements, so the completed arrangement has the appearance represented in the table.

The relation of properties of elements to atomic weights. There is evidently a close relation between the properties of an element and its atomic weight. For example, consider the elements in the first horizontal row. Helium is an inert element. Following it, lithium is a metallic element, has a valence of 1, and possesses a strong base-forming character. The next element, glucinum, has a valence of 2, and is less strongly base-forming, while boron has some base-forming and some acid-forming properties. In carbon, all base-forming properties have disappeared, and the acid-forming properties are more marked than in boron. These become still more emphasized as we pass through nitrogen and oxygen, until on reaching fluorine we have one of the strongest acid-forming elements. The properties of these eight elements vary regularly with their atomic weights, or, in mathematical language, are *continuous functions* of them.

The periodic law. If it were true that helium had the smallest atomic weight of any of the elements and fluorine the greatest, so that in passing from one to the other we included all the elements, we could say that the properties of elements were *continuous* functions of their atomic weights. But fluorine is an element of relatively small atomic weight, and the one following it, neon, breaks the regular order, for in it reappear all the characteristic properties of helium. Sodium, following neon, bears much

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

PERIODS	GROUP 0		GROUP I		GROUP II		GROUP III		GROUP IV		GROUP V		GROUP VI		GROUP VII		GROUP VIII
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	
1	He = 3.99		Li = 6.94		Gl = 9.1		B = 11		C = 12.005		N = 14.01		O = 16		F = 19		
2		Ne = 20.2		Na = 23		Mg = 24.32		Al = 27.1		Si = 28.3		P = 31.04		S = 32.06		Cl = 35.46	
3	A = 39.88		K = 39.1		Ca = 40.07		Sc = 44.1		Ti = 48.1		V = 51		Cr = 52		Mn = 54.93		Fe = 55.84 Co = 58.97 Ni = 58.68
4				Cu = 63.57		Zn = 65.37		Ga = 69.9		Ge = 72.5		As = 74.96		Se = 79.2		Br = 79.92	
5	Kr = 82.92		Rb = 85.45		Sr = 87.63		Y = 89		Zr = 90.6		Cb = 93.5		Mo = 96				Ru = 101.7 Rh = 102.9 Pd = 106.7
6				Ag = 107.88		Cd = 112.4		In = 114.8		Sn = 118.7		Sb = 120.2		Te = 127.5		I = 126.92	
7	X = 130.2		Cs = 132.81		Ba = 137.37		La = Lu* 139.0 – 175.0		Ce = 140.25		Ta = 181.5		W = 184				Os = 190.9 Ir = 193.1 Pt = 195.2
8				Au = 197.2		Hg = 200.6		Tl = 204		Pb = 207.2		Bi = 208					
9	Nt = 222.4				Ra = 226				Th = 232.4				U = 238.2				
Formula of oxide Formula of hydride			R_2O RH		RO RH_2		R_2O_3 RH_3		RO_2 RH_4		R_2O_5 RH_3		RO_3 RH_2		R_2O_7 RH		RO_4

---

* This includes a number of elements whose atomic weights lie between 140 and 173, but which have not been accurately studied, and so their proper arrangement is uncertain. They do not fit into the table in its present form.

the same relation to lithium that neon does to helium, and the properties of the elements in the second row vary much as do the properties of the elements in the first row, until argon is reached, when another repetition begins. The properties of the elements do not vary continuously, therefore, with atomic weights, but at regular intervals there is a repetition, or *period.* This generalization is known as the *periodic law*, and may be stated thus: *The properties of elements are periodic functions of their atomic weights.*

Two families in a group. The elements of each group (excepting Group 0) fall naturally into two families. The elements in the odd-numbered horizontal rows (called *periods*) form one *family*, those in the even-numbered periods, the other. In the table these are arranged under the headings *A* and *B*. The elements in one family are much more similar to each other than they are to those in the other family in the same group. Thus, magnesium, zinc, cadmium, and mercury form one family of very similar elements in Group II, while glucinum, calcium, strontium, barium, and radium form the other.

Family resemblances. Let us inquire more closely in what respects the elements of a family resemble each other.

1. ***Valence.*** In general the valence of the elements in a family is the same, and the formulas of their compounds are therefore similar. If we know that the formula of sodium chloride is NaCl, it is pretty certain that the formula of potassium chloride will be KCl — not KCl_2 nor KCl_3. The general formulas R_2O, RO, etc., placed below the columns, indicate the formulas of the oxides of the elements in the column, provided they form oxides. In like manner the formulas RH, RH_2, etc. show the composition of the compounds formed with hydrogen or with chlorine.

2. *Chemical conduct.* The chemical characteristics of the members of a family are quite similar. If one member is a metal, the others usually are; if one is a nonmetal, so, too, are the others. The families in Group I and Group II consist of metals, while the elements found in Group VI and Group VII form acids. There is in addition a certain regularity in properties of the elements in each family. If the element at the head of the family is a strong acid-forming element, this property is likely to diminish gradually, as we pass to the members of the family with higher atomic weights. Thus, phosphorus is strongly acid-forming, arsenic less so, and antimony still less so, while bismuth has almost no acid-forming properties. As a result of this regularity, the elements of high atomic weight at the bottom of the family columns are nearly all metals in their chemical conduct. We shall meet with many illustrations of this fact.

3. *Physical properties.* In the same way, the physical properties of the members of a family show a gradation as we pass from element to element in the family. Thus, the densities of the members of the magnesium family are

$$\mathrm{Mg} = 1.75,\ \mathrm{Zn} = 7.00,\ \mathrm{Cd} = 8.67,\ \mathrm{Hg} = 13.6$$

Their melting points are

$$\mathrm{Mg} = 651^\circ,\ \mathrm{Zn} = 419.4^\circ,\ \mathrm{Cd} = 320.9^\circ,\ \mathrm{Hg} = -38.9^\circ$$

Value of the periodic law. The periodic law has proved of much value in the development of the science of chemistry.

1. *It simplifies study.* It is at once evident that such regularities very much simplify the study of chemistry. A thorough study of one element of a family makes the study of the other members a much easier task, since so

many of the properties and chemical reactions of the elements are similar. Thus, having studied the element sulfur in some detail, it is not necessary to study selenium and tellurium so closely, for most of their properties can be predicted with a fair degree of accuracy from the relation which they sustain to sulfur.

2. ***It predicts new elements.*** When the periodic law was first formulated there were several vacant places in the table which evidently belonged to elements at that time unknown. From their position in the table, Mendeléeff predicted with great precision the properties of the elements which he felt sure would one day be discovered to fill these places. Three such elements — scandium, germanium, and gallium — were found within fifteen years, and their properties agreed in a remarkable way with the predictions of Mendeléeff. This is shown in the following table, in which the properties of gallium are compared with those which Mendeléeff predicted:

PROPERTIES OF GALLIUM	PREDICTED	FOUND
Atomic weight	about 69	69.9
Melting point	low	30°
Specific gravity	5.9	5.95
Formula of oxide	R_2O_3	Ga_2O_3
Action of air	no action	only slight, even at red heat

According to the table there are still some undiscovered elements, and much effort has been made to find them. In the family with manganese there should be an element of atomic weight approximately 100, and another of about 187. There are also two vacant places in the last period.

3. *It indicates probable errors.* The physical constants of many of the elements did not at first agree with those demanded by the periodic law, and a further study of many such cases showed that errors had been made. The law has therefore done much service in indicating probable error.

Imperfections of the periodic table. There still remain a good many features which must be regarded as imperfections in the table. Most conspicuous is the fact that the element hydrogen has no place in it. In some of the groups elements appear in one of the families, while all of their properties show that they belong in the other. Thus, sodium belongs with lithium and not with copper; fluorine belongs with chlorine and not with manganese. There are three instances where the elements must be transposed in order to make them fit into their proper group. According to their atomic weights, tellurium should follow iodine, argon should follow potassium, and nickel should follow cobalt. Their properties show in each case that this order must be reversed. The table separates some elements altogether which in many respects have closely agreeing properties. Iron, chromium, and manganese are in different groups, although they are similar in many respects.

The system is therefore to be regarded as but a partial and imperfect expression of some very important and fundamental relation between the substances which we know as elements, the exact nature of this relation being as yet not completely clear to us. The knowledge gained in recent years from the study of radium and similar elements (Chapter XLII) has given us some insight into the nature of this relationship, but it would take us too far to pursue the matter to greater detail.

EXERCISES

1. Suppose that an element were discovered that filled the blank in Group 0, Period 4; what properties would it probably have?

2. Suppose that an element were discovered that filled the blank in Group VI, Period 8, family *B*; what properties would it have?

3. Sulfur and oxygen both belong in Group VI, although in different families; in what respects are the two similar?

4. Consult encyclopedia for some of the notable events in the life of Mendeléeff.

5. What processes of nature can you think of that you would call periodic?

6. Can you think of any mechanical processes that illustrate a periodic function?

CHAPTER XXII

THE CHLORINE FAMILY

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . .	19.00	– 223°	– 187°	pale-yellowish gas
Chlorine (Cl) . .	35.46	– 101.5°	– 33.6°	greenish-yellow gas
Bromine (Br) . .	79.92	– 7.3°	63°	red liquid
Iodine (I) . . .	126.92	113.5°	184.4°	purplish-black solid

NOTE. Chlorine, as well as hydrogen chloride and hydrochloric acid, has been described in Chapter XIV, and that chapter should be reviewed in connection with the general study of the chlorine family.

The family. The four elements named in the above table form a strongly marked family of elements and illustrate very clearly the way in which the members of a family in a periodic group resemble each other, as well as the character of the differences which we may expect to find between the individual members.

1. ***Occurrence.*** These elements do not occur in nature in the free state. The compounds of the last three elements of this family are found extensively in sea water, and on this account the name *halogens*, signifying "producers of sea salt," is sometimes applied to the family.

2. ***Properties.*** By reference to the table it will be seen that the melting point and the boiling point of the elements of this family increase with their atomic weights. A somewhat similar gradation is noted in their color and state. The affinity of these elements for hydrogen and the

metals is in the inverse order of their atomic weights, fluorine having the strongest affinity and iodine the weakest. Only chlorine and iodine form oxides, and those of the former element are very unstable.

3. ***Compounds with hydrogen.*** Hydrogen combines with each of the elements of the family to form the following important hydrides:

Hydrogen fluoride (H_2F_2): a colorless liquid boiling at 19.4°.
Hydrogen chloride (HCl): a colorless gas liquefying at − 83.1°.
Hydrogen bromide (HBr): a colorless gas liquefying at − 73°.
Hydrogen iodide (HI): a colorless gas liquefying at − 34.1°.

In the complete absence of water these hydrides are rather inactive and have neither acid nor basic properties. They dissolve in water, however, forming solutions that are acid in character.

FLUORINE

Occurrence. Fluorine occurs in nature most abundantly in the mineral fluorite (CaF_2), in cryolite (Na_3AlF_6), and in the complex mineral fluorapatite, $3\,Ca_3(PO_4)_2 \cdot CaF_2$. Traces of compounds of fluorine are also found in many other minerals, in sea water, in bones, and in the enamel of the teeth.

Preparation. While the compounds of fluorine have been known for a long time, all attempts to isolate the free element resulted in failure until 1886, when the French chemist Moissan (Fig. 103) succeeded in obtaining it in a pure state. He prepared it by the electrolysis of hydrogen fluoride in which had been dissolved a little potassium hydrogen fluoride (KHF_2) to render the liquid an electrolyte. The solution was placed in a U-shaped tube (Fig. 104) made of platinum (or copper), which was furnished with electrodes and exit tubes for the escape of the fluorine and hydrogen which are liberated, the former at the anode and the other at the cathode. Since hydrogen fluoride boils at 19.4°, the process must be carried out at a low temperature to prevent the liquid from vaporizing.

Properties and conduct. Fluorine is a gas, slightly yellow in color, and is 1.3 times as heavy as air. It can be obtained in the form of a yellow liquid which boils at – 187° and solidifies at – 223°. Chemically, it is one of the most active of all elements. Most of the elements, when brought in contact with fluorine, combine with it with so much energy as to produce light. It unites with hydrogen with explosive violence and readily abstracts it from its compounds. For example, it decomposes water with great energy, forming hydrogen fluoride and oxygen:

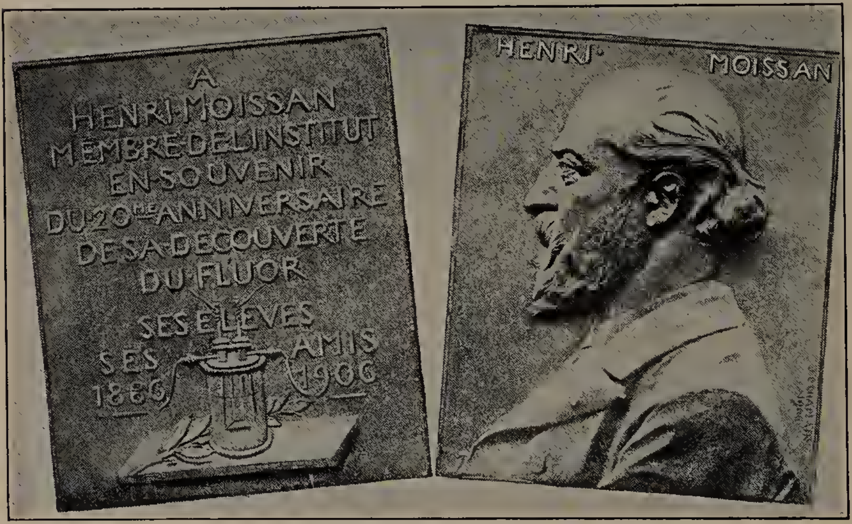


FIG. 103. Tablet erected by the associates and friends of Moissan, in his laboratory in Paris, in 1906, on the twentieth anniversary of the isolation of fluorine

$$2\,F_2 + 2\,H_2O \longrightarrow 2\,H_2F_2 + O_2 + 2 \times 6800 \text{ cal.}$$

It liberates all the other members of the chlorine family from their compounds with hydrogen and the metals. It does not combine with oxygen, however, and but superficially attacks gold, platinum, or copper.

Hydrogen fluoride (H_2F_2). Hydrogen fluoride is readily obtained from fluorite by the action of concentrated sulfuric acid. The equation is as follows:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$

The formula is usually written H_2F_2, although by selecting the proper temperature the compound may be obtained in any of the forms indicated by the formulas HF, H_2F_2, H_3F_3. In its properties hydrogen fluoride resembles the hydrides of the other elements of this family, although it is more easily condensed to a liquid. It boils at 19.4° and can therefore be liquefied at ordinary pressures. It is soluble in all proportions in water, forming *hydrofluoric acid.* Its fumes are exceedingly irritating to the respiratory organs, and several chemists have lost their lives by accidentally breathing them.

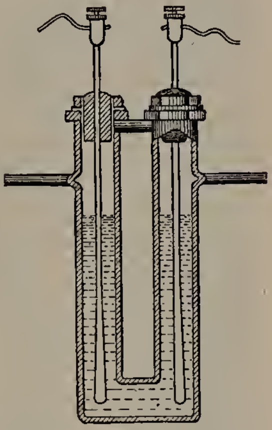


FIG. 104. A metal U-tube for the preparation of fluorine

Hydrofluoric acid. Hydrofluoric acid, like other acids, readily acts on bases and metallic oxides and forms the corresponding *fluorides.* It acts very vigorously upon organic matter, a single drop of the concentrated acid making a sore on the skin which is slow in healing and very painful. Its most characteristic property is its action upon silicon dioxide (SiO_2), with which it forms water and the gas silicon tetrafluoride (SiF_4), as shown in the equation

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4 + 2\,H_2O$$

Glass consists of certain compounds of silicon which are likewise acted on by the acid, so that it cannot be kept in glass bottles. It is preserved in flasks made of a wax derived from petroleum and known as ceresin (Fig. 105). Ordinary commercial hydrofluoric acid contains about 50 per cent of hydrogen fluoride.

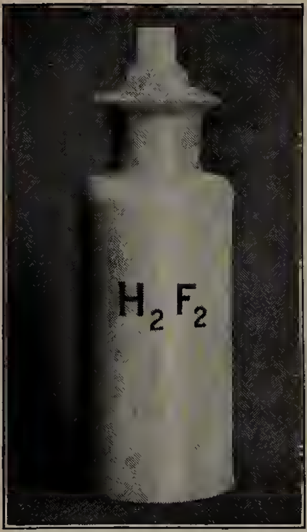


Fig. 105. A bottle made out of ceresin, for holding hydrofluoric acid

Etching. The action of hydrofluoric acid on silicon compounds is taken advantage of to etch designs upon glass. The glass is painted over with a protective paint upon which the acid will not act, the parts which it is desired to make opaque being left unprotected. A mixture of fluorite and sulfuric acid is then painted over the vessel, and after a few minutes is washed off. Wherever the hydrofluoric acid comes in contact with the glass it acts upon it, destroying its luster and making it opaque, so that the exposed design will be etched upon the clear glass. Frosted glass globes are often made in this way, but more frequently by a sand blast. The etching may also be accomplished by covering the glass with a thin layer of paraffin, cutting the design through the wax, and then exposing the glass to the fumes of the gas.

BROMINE

History and occurrence. Bromine was discovered in 1826 by the French chemist Ballard, who isolated it from sea salt. It occurs almost entirely in the form of sodium bromide ($NaBr$) and magnesium bromide ($MgBr_2$), which are found in many springs and salt deposits.

The Stassfurt deposits in Germany and the salt waters of Michigan and Ohio are especially rich in bromides.

Preparation of bromine. The laboratory and the commercial method for preparing bromine are as follows:

1. ***Laboratory method.*** Just as chlorine is liberated by the action of hydrochloric acid on manganese dioxide (p. 159), so bromine may be liberated by a similar reaction, by using hydrobromic acid in place of hydrochloric:

$$4\,HBr + MnO_2 \longrightarrow MnBr_2 + Br_2 + 2\,H_2O$$

Since hydrobromic acid is unstable, it is more convenient to generate it in the course of the reaction by using a mixture of sodium bromide and sulfuric acid. The equation for the complete reaction is as follows:

$$2\,NaBr + 2\,H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

The materials are placed in a retort *A*, arranged as shown in Fig. 106. The end of the retort just touches the water in the flask *B*, which is partially immersed in ice water. As the contents of the retort are heated the bromine distills over, and is collected in the cold receiver.

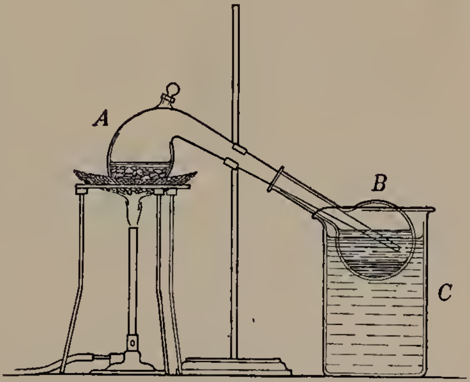


FIG. 106. An apparatus for the preparation of bromine in the laboratory

2. ***Commercial method.*** In the United States bromine is obtained commercially from salt water; the bromine is liberated by electrolysis. Some chlorine is also set free in the process, but this reacts with the bromides present in the water; thus,

$$2\,NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2$$

Properties. Bromine is a dark-red liquid whose density is 3.102. Its vapor has an offensive odor and is very irritating to the eyes and throat. The liquid boils at 63° and solidifies at – 7.3°, but even at ordinary temperatures it has a high vapor pressure, forming a reddish-brown gas very similar to nitrogen dioxide in appearance. 100 volumes of water dissolves about 1 volume of bromine at 20°, forming a reddish solution called bromine water. Bromine is much more readily soluble in carbon disulfide.

Chemical conduct and uses. In chemical conduct bromine is very similar to chlorine, except that it is less active. It combines directly with many of the same elements with which chlorine unites, but with less energy. It combines with hydrogen, and even abstracts it from some of its compounds. As would be expected, its bleaching action is much less marked than that of chlorine. Its solution in water is often used as an oxidizing agent.

Bromine is used chiefly in the preparation of bromides, which are employed to a considerable extent in photography and as medicinal agents. It is likewise used in the preparation of a number of organic drugs and dyestuffs.

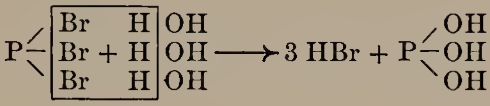
Hydrogen bromide (HBr). When sulfuric acid acts upon a bromide, hydrogen bromide is set free:

$$2\,NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HBr$$

At the same time some bromine is liberated, as may be seen from the red fumes which appear and from the odor. The explanation of this is found in the fact that hydrogen bromide is much *less stable* than hydrogen chloride and is therefore *more easily oxidized.* Concentrated sulfuric acid is a good oxidizing agent (p. 247) and oxidizes a part of the hydrogen bromide, liberating bromine:

$$H_2SO_4 + 2\,HBr \longrightarrow H_2O + H_2SO_3 + Br_2$$

The pure compound is best prepared by the action of water upon phosphorus tribromide, in which reaction hydrogen bromide and phosphorous acid, $P(OH)_3$ (or H_3PO_3), are formed. The reaction is made clearer by the use of structural formulas:



The preparation of hydrogen bromide is conducted as follows: Red phosphorus, together with enough water to cover it, is placed in the flask *A* (Fig. 107), and bromine is put into the dropping funnel *B*. By means of the stopcock the bromine is allowed to flow drop by drop into the flask, the reaction taking place without the application of heat. The phosphorus and bromine unite to form PBr_3, which then reacts with the water as expressed in the above equation. The U-tube *C* contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus in the U-tube. The hydrogen bromide is collected in *D* by displacement of air, or an aqueous solution of it may be prepared as was done in the case of hydrogen chloride (Fig. 78).

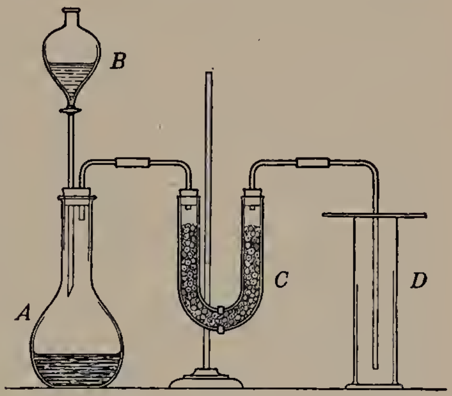


FIG. 107. The preparation of hydrogen bromide

Properties and conduct. Hydrogen bromide is very similar to hydrogen chloride in its properties. It is a colorless gas and is very soluble in water, 1 volume of water dissolving

612 volumes of the gas under standard conditions. It differs from hydrogen chloride mainly in the fact that it is more readily oxidized. Even the oxygen of the air gradually acts upon it to form water and free bromine.

The aqueous solution of hydrogen bromide is known as *hydrobromic acid.* This acid has properties similar to those of hydrochloric acid, but it is less stable. It reacts with metals, their oxides, and their hydroxides to form bromides.

IODINE

History and occurrence. Iodine is present in sea water, but in relatively small quantities. Certain seaweeds absorb the iodine from the water, in this way concentrating it within their tissues. It was from the ashes obtained by the burning of seaweed that the French chemist Courtois, in 1812, first isolated the element. Iodine is found in certain sponges, oysters, and fishes, but its chief source is from the deposits of Chile saltpeter (sodium nitrate). It is interesting to note that small amounts of iodine exist in the human body in the thyroid gland.

Preparation. Iodine may be prepared in a number of ways, the principal methods being the following:

1. ***Laboratory method.*** Iodine can readily be prepared in the laboratory from an iodide by the method used in preparing bromine (Fig. 106), except that sodium iodide is substituted for sodium bromide. It can also be prepared by passing chlorine into a solution of an iodide:

$$Cl_2 + 2\,NaI \longrightarrow 2\,NaCl + I_2$$

2. ***Commercial method.*** Formerly iodine was obtained entirely from the ashes of seaweeds. While a small amount of the element is still obtained from this source, by far the

largest supply comes from crude Chile saltpeter. It is present in these deposits in the form of sodium iodate ($NaIO_3$) and is liberated by the action of the sulfites of sodium:

$$2\,NaIO_3 + 3\,Na_2SO_3 + 2\,NaHSO_3 \longrightarrow 5\,Na_2SO_4 + H_2O + I_2$$

Properties. Iodine is a purplish-black shining solid which, when sublimed, crystallizes in brilliant plates. It has a density of 4.95, melts at 113.5°, and boils at 184.4°. The element has a strong, unpleasant odor, although the odor is not so disagreeable as that of chlorine or bromine. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases in amount as heat is applied. It is only slightly soluble in water, 1 part being soluble in 3750 parts of water at 15°. It is very soluble in a solution of potassium iodide or of hydrogen iodide, forming a dark-brown solution. It also dissolves in carbon disulfide, forming a violet-colored solution.

Chemical conduct and uses. Chemically, iodine is quite similar to chlorine and bromine, but is still less active than bromine. Both chlorine and bromine displace it from its salts:

$$2\,KI + Br_2 \longrightarrow 2\,KBr + I_2$$
$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

When even minute traces of iodine are added to thin starch paste a very intense blue color develops, and this reaction forms a delicate test for iodine. A solution of iodine in alcohol is called *tincture of iodine* and is extensively used in medicine. Iodine is also largely used in the preparation of iodides and of certain dyes and organic drugs. Iodoform, a common antiseptic, has the formula CHI_3.

Hydrogen iodide. This compound is still less stable than hydrogen bromide; it follows, therefore, that it cannot be prepared by the action of sulfuric acid upon an iodide

(p. 270). It is prepared by a method similar to that used in the preparation of hydrogen bromide; namely, by the action of phosphorus triiodide on water. An aqueous solution of the gas is easily prepared by passing hydrogen sulfide into water in which finely divided iodine is suspended:

$$H_2S + I_2 \longrightarrow 2\,HI + S$$

The hydrogen iodide dissolves in the water as fast as formed, while the sulfur is precipitated and is removed by filtration.

Properties of hydrogen iodide. Hydrogen iodide resembles hydrogen chloride and hydrogen bromide in its physical properties, being a strongly fuming colorless gas. It is 4.37 times as heavy as air. At 10° about 450 volumes of the gas dissolves in 1 volume of water. Owing to the ease with which the gas is decomposed into its elements, it acts in many respects like nascent hydrogen, being a strong reducing agent. This might be expected from the fact that it is an endothermic compound, as shown in the equation

$$H_2 + I_2 \longrightarrow 2\,HI - 12{,}072 \text{ cal.}$$

The solution of hydrogen iodide in water has strong acid properties and is known as *hydriodic acid.*

Chemical conduct of hydriodic acid. Hydriodic acid differs from hydrochloric acid and hydrobromic acid mainly in the ease with which it is oxidized. The freshly prepared solution is colorless, but soon turns brown, owing to the liberation of iodine by the oxygen of the air:

$$4\,HI + O_2 \longrightarrow 2\,H_2O + 2\,I_2$$

As the action continues, the iodine separates in crystalline form. The acid, as well as hydrogen iodide, is therefore a strong reducing agent.

Hydriodic acid reacts with many of the metals, as well as with their oxides and hydroxides, to form the corresponding salts.

Salts of hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydriodic acid: fluorides, chlorides, bromides, iodides. Many of these salts are well-known compounds and have important uses. They can be prepared by the usual methods for preparing salts; namely, by the action of the acid upon the metals directly or upon their oxides or hydroxides. The most important fluoride is the well-known calcium fluoride (CaF_2), or *fluorite.* The chlorides, bromides, and iodides resemble each other closely in their properties. They are all soluble in water except the silver, lead, and mercurous salts. Sodium chloride is the most important of the chlorides. Potassium bromide and potassium iodide are used in medicine, while silver bromide and iodide are largely used in photography.

THE OXYGEN COMPOUNDS OF THE HALOGENS

The halogens have but little affinity for oxygen, only chlorine and iodine forming oxides. While several oxygen acids are known, with few exceptions these are unstable and exist only in dilute solution. Both the acids and their salts readily give up oxygen. They are therefore good oxidizing agents and are used chiefly for this purpose.

The oxides. Chlorine forms three oxides; namely, Cl_2O, Cl_2O_7, and ClO_2. They are difficult to prepare and very unstable. Iodine forms two oxides, of the formulas I_2O_4 and I_2O_5. The latter, known as iodine pentoxide, is the best-known oxide of the group. It is a white solid and is fairly stable, although it is decomposed into iodine and oxygen when heated.

The oxygen acids. The most important of the oxygen acids of the halogens are the following:

1. ***Hypochlorous acid* ($HClO$).** This acid is unstable and has been obtained only in dilute solutions. Its salts, known as the *hypochlorites*, may be prepared by passing chlorine into the *cold* solutions of the hydroxides of the metals. Thus, potassium hypochlorite ($KClO$) is formed as indicated in the following equation:

$$2\,KOH + Cl_2 \longrightarrow KClO + KCl + H_2O$$

Both the acid and its salts easily give up their oxygen and are therefore good oxidizing agents.

2. ***Chloric acid* ($HClO_3$).** This acid is more stable than hypochlorous acid, but has not been obtained in a pure state. Its salts, the *chlorates*, may be prepared by passing chlorine into a *hot* solution of the hydroxides of the metals. Potassium chlorate, for example, is easily obtained by passing chlorine into a hot concentrated solution of potassium hydroxide:

$$3\,Cl_2 + 6\,KOH \longrightarrow KClO_3 + 5\,KCl + 3\,H_2O$$

The chlorates are excellent oxidizing agents. Sodium chlorate and potassium chlorate are chiefly used in the preparation of explosives, fireworks, and oxygen.

Preparation of hypochlorites and chlorates by electrolytic methods. It will be recalled that the electrolysis of solutions of potassium chloride or of sodium chloride results in the formation of chlorine, together with the corresponding hydroxides of metals. It is possible so to regulate this process that the chlorine, instead of being evolved, is retained in the solution, together with the hydroxides, with which it acts to form hypochlorites or chlorates, according to the equations given above. This method is now coming into general use for the preparation of these salts. It is possible to obtain either the hypochlorites or the chlorates by properly choosing the conditions of the electrolysis.

3. ***Perchloric acid* ($HClO_4$).** This acid is likewise unstable, although it is possible to obtain it in a pure state. It is a colorless liquid, and sometimes decomposes with great violence. Potassium perchlorate, the best known of its salts, is a white solid and, like the salts of other oxygen acids of chlorine, is an excellent oxidizing agent.

Hypobromous acid ($HBrO$) and bromic acid ($HBrO_3$), the analogues of hypochlorous acid and chloric acid have also been prepared in dilute solution. The acids, as well as their salts, are similar to the corresponding chlorine compounds. Iodic acid (HIO_3) and periodic acid (H_5IO_6) are also known. They are both white solids. The acids, as well as their salts, are strong oxidizing agents.

EXERCISES

1. How do we account for the fact that liquid hydrogen fluoride does not conduct the electric current?

2. Why is sulfuric acid used for liberating hydrogen fluoride from fluorite?

3. Why is the formula for hydrogen fluoride written H_2F_2, while that of hydrogen chloride is written HCl?

4. What discoveries made by Moissan have been noted other than the preparation of fluorine?

5. Cl_2O is the anhydride of what acid?

6. A solution of hydrogen iodide on standing turns brown. How is this accounted for?

7. How can bromine vapor and nitrogen dioxide be distinguished from each other?

8. Write the equations for the reaction which takes place when hydrogen iodide is prepared from iodine, phosphorus, and water.

9. From their behavior toward sulfuric acid, to what class of agents do hydrobromic acid and hydriodic acid belong?

10. Give the derivation of the names of the elements of the chlorine family.

11. Write the names and formulas for the binary acids of the chlorine group in the order of the stability of the acids.

12. What is formed when a metal dissolves in each of the following: nitric acid; dilute sulfuric acid; concentrated sulfuric acid; hydrochloric acid; aqua regia?

13. How could you distinguish between a chloride, a bromide, and an iodide?

14. In what respects are the elements included in the chlorine family similar?

15. What weight of sodium chloride is necessary to prepare sufficient hydrogen chloride to saturate 1 l. of water under standard conditions?

16. What weight of fluorite is necessary for the preparation of 1 kg. of the commercial hydrofluoric acid?

17. The concentrated hydrochloric acid of commerce has a density of 1.20 and contains 40 per cent of hydrogen chloride. What weights of salt and sulfuric acid are necessary to prepare 100 kg. of this acid?

18. What weights of chlorine and potassium hydroxide are necessary for the preparation of 1 kg. of potassium chlorate? Does this process appeal to you as an economical method of preparation?

19. What substances so far studied are used as bleaching agents? To what is the bleaching action of each due?

20. On decomposition 100 l. of hydrogen chloride would yield how many liters of hydrogen and of chlorine respectively?

CHAPTER XXIII

MOLECULAR WEIGHTS; ATOMIC WEIGHTS

Introduction. In early chapters two problems were left unsolved for the reason that their solution requires a wider acquaintance with chemical facts and laws than had been gained when the problems were suggested.

1. ***Molecular weights.*** In Chapter VIII it was shown that from the results of the careful analysis of a compound it is easy to calculate a formula, provided we have a system of atomic weights and provided *we adopt the simplest formula possible.* The method described would lead to the formula HO for hydrogen peroxide, whereas the true formula might be H_2O_2 or H_3O_3. To decide between these it is necessary to know the molecular weight of the compound. If it is approximately 17, the simple formula is correct. If it is approximately 34, the true formula is H_2O_2.

2. ***The selection of the atomic weight from the combining weights.*** In Chapter VII we found that it is easy to determine a combining weight for each element; but that many elements have more than one combining weight, the one a multiple of the other. Thus, the analysis of water shows that if we take hydrogen as unity, the combining weight of oxygen is 7.94, while the analysis of hydrogen peroxide gives the combining weight of oxygen as 15.88. It is therefore a question of which combining weight is to be selected as the true atomic weight. The clue to the solution of these two problems is found in a great generalization known as *Avogadro's hypothesis.*

Gay-Lussac's law of volumes. Before considering Avogadro's hypothesis, however, it is essential for us to have in mind a law first pointed out by Gay-Lussac (Fig. 28), and known as the law of volumes.

In the discussion of the composition of hydrogen chloride it was stated that *1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.* With bromine and iodine similar combining ratios hold good. These facts recall the simple volume relations already noted in the study of the composition of steam (p. 78) and ammonia (p. 206). These relations may be represented graphically in the following way, the rectangles representing *equal volumes*:

$$\boxed{\mathrm{H_2}} + \boxed{\mathrm{Cl_2}} \longrightarrow \boxed{\mathrm{HCl}} + \boxed{\mathrm{HCl}}$$

$$\boxed{\mathrm{H_2}} \quad \boxed{\mathrm{H_2}} + \boxed{\mathrm{O_2}} \longrightarrow \boxed{\mathrm{H_2O}} + \boxed{\mathrm{H_2O}}$$

$$\boxed{\mathrm{H_2}} \quad \boxed{\mathrm{H_2}} \quad \boxed{\mathrm{H_2}} + \boxed{\mathrm{N_2}} \longrightarrow \boxed{\mathrm{NH_3}} + \boxed{\mathrm{NH_3}}$$

In the early part of the past century Gay-Lussac studied the volume relations of many combining gases, and concluded that similar relations *always* hold. His observations are summed up in the following generalization, known as the law of volumes: *When two gases combine chemically there is always a simple ratio between their volumes, and also between the volume of either one of them and that of the product, provided it is a gas.* By a simple ratio is meant, of course, the ratio of integer numbers, as 1 : 2, or 2 : 3.

The relations expressed in the law of volumes are so simple and so unexpected that we at once feel that they indicate a very simple ratio between the number of molecules present in equal volumes of gases. As early as 1811 the Italian physicist Avogadro (Fig. 108) suggested that the ratios become perfectly intelligible if we assume that *equal volumes of any two gases contain the same number of molecules.* This generalization is known as the *hypothesis of Avogadro*, and it is in complete accord with all that we have learned about gases since Avogadro's time.

Avogadro's hypothesis, and molecular weights. Assuming the truth of Avogadro's hypothesis, we have a simple means of deciding upon the *relative* weights of the various kinds of molecules; for if equal volumes of two gases contain the *same number of molecules*, the weights of the two kinds of molecules must be in the same ratio as the weights of the two volumes made up of these molecules.

Fig. 108. Statue erected at Turin, Italy, to the memory of Avogadro

For example, the weight of a liter of ammonia is 0.7708 g. and that of a liter of hydrogen chloride is 1.6398 g. These values will therefore indicate the *relative* weights of the two kinds of molecules if there is the same number of each in a liter. If we adopt some one gas as a standard, we can readily determine the weights of all gaseous molecules relatively to those of the standard gas. Thus, if we adopt ammonia as standard (unity), the molecule of hydrogen chloride is 2.14 times as heavy as the standard.

Oxygen as standard. It will be seen that the gas selected as standard and the volume chosen for comparison will make no difference, since the weights are all *relative* in any case. But since the molecules are all made up of atoms, it is important that the standard chosen for atomic weights should be in accord with that chosen for molecular weights. For many reasons oxygen serves best for atomic weights, and it is also chosen for molecular weights.

Relative weights of molecules of oxygen and of hydrogen. In Chapter VII we saw that 8 is the smallest integer that can be assigned as the combining weight of oxygen without making the combining weight of hydrogen less than 1.

Now the weight of 1 l. of oxygen is 1.429 g. and that of 1 l. of hydrogen is 0.08987 g. Making oxygen 8, the *ratio* of these two weights is 8 : 0.504 or 16 : 1.008, and according to Avogadro's hypothesis *these numbers must represent the weights of the two kinds of molecules.* If we can now decide upon how many atoms are in the molecule of oxygen and in that of hydrogen, we can at once decide whether to make the standard of atomic weights the atom of oxygen at 16 or at 8.

Two atoms in the molecule of oxygen and of hydrogen. We have seen that when hydrogen and chlorine combine, the *ratio by volume* is expressed in the equation

$$\text{1 volume hydrogen} + \text{1 volume chlorine} \longrightarrow \text{2 volumes hydrogen chloride}$$

Therefore, according to Avogadro's hypothesis,

$$\text{1 molecule hydrogen} + \text{1 molecule chlorine} \longrightarrow \text{2 molecules hydrogen chloride}$$

But every molecule of hydrogen chloride must contain *at least* 1 atom; therefore, since 2 molecules of hydrogen chloride are formed from 1 molecule of hydrogen, each molecule of hydrogen must contain *at least* 2 atoms.

When hydrogen and oxygen combine to form steam, the ratio by volume is expressed in the equation

$$2 \text{ volumes hydrogen} + 1 \text{ volume oxygen} \longrightarrow 2 \text{ volumes steam}$$

Therefore, according to Avogadro's hypothesis,

$$2 \text{ molecules hydrogen} + 1 \text{ molecule oxygen} \longrightarrow 2 \text{ molecules steam}$$

But each molecule of steam has *at least* 1 atom of oxygen, and since 2 molecules of steam are formed from 1 molecule of oxygen, the molecule of oxygen must contain *at least* 2 atoms.

There are no facts known that suggest that the molecule of either hydrogen or oxygen contains *more* than two atoms, and so we adopt the formulas H_2 and O_2 for these gases.

Oxygen atom, 16; oxygen molecule, 32. Since the weights of equal volumes of oxygen and hydrogen (1 l. each) are in the ratio of 16 : 1.008, the weights of the individual molecules are in the same ratio. And since the two kinds of molecules each contain two atoms, the weights of the two kinds of atoms are also in the ratio 16 : 1.008. Consequently, if we wish to have the atomic weight of hydrogen greater than unity, we must adopt the weight 16 and not 8 for the atomic weight of oxygen. Since the molecule of oxygen consists of 2 atoms, we must adopt the weight 32 for the oxygen molecule.

Molecular weights from weight of 1 liter. We have now devised a method of determining how much heavier one kind of molecule is than another, and have fixed upon the weight of one standard molecule (oxygen), with which all others can be compared. The determination of molecular weights now becomes easy. For example, 1 l. of oxygen weighs 1.429 g., while 1 l. of hydrogen chloride weighs 1.6398 g. The ratio between the weights of the two kinds of molecules is therefore 1.429 : 1.6398. To compare the hydrogen chloride molecule with oxygen taken as 32 we need only solve the proportion: $1.429 : 1.6398 = 32 : x$. The molecular weight of hydrogen chloride (x) is therefore 36.7.

Gram-molecular volume equals 22.4 liters. Having adopted 32 as the standard for oxygen, it is of interest to find the volume occupied by the gram-molecular weight of this gas; namely, 32 g. This volume will evidently be $32 \div 1.429$, or *22.4 l.* If we construct a vessel of exactly this content and fill it with oxygen gas, it will contain just enough molecules of oxygen to weigh 32 g., which is our standard weight for oxygen.

If now we replace the oxygen by another gas, say, hydrogen chloride, we shall have the same number of molecules present. The weight of hydrogen chloride filling the vessel is 36.45 g. But since there is the same number of molecules, the values 32 and 36.45 must represent the relative weights of the two kinds of molecules. In like manner, the weight of 22.4 l. of *any* gas will give a number which expresses the weight of a molecule of that gas compared with the molecule of oxygen taken as the standard. These relations are illustrated in Fig. 109. We therefore reach the following simple rule: *The molecular weight of any gas may be found by determining the weight in grams of 22.4 l. of the gas.* The volume 22.4 l. is called the *gram-molecular volume* of gases. Owing to the fact that most gases do not exactly conform to any of the gas laws, the weight of 22.4 l. of a gas is not its *precise* molecular weight, but is very close to it.

Other methods of determining molecular weights. It will be noticed that Avogadro's hypothesis gives us a method by which we can determine the relative weights of the molecules of two gases *because it enables us to tell when we are dealing with an equal number of the two kinds of molecules.* If by any other convenient means we can get this information, we can make use of the knowledge so gained to determine the molecular weights of the two substances.

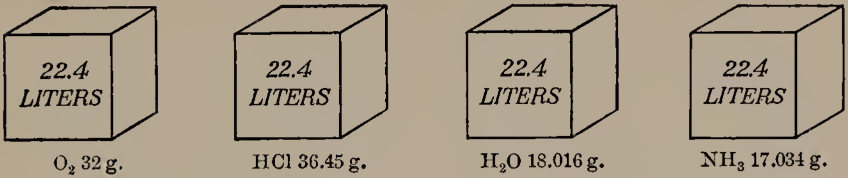


FIG. 109. The weight of 22.4 l. of various gases

Raoult's laws. Two laws have been formulated which give us just such information. They are known as Raoult's laws and can be stated as follows:

1. *When weights of substances which are proportional to their molecular weights are dissolved in the same weight of a solvent, the rise of the boiling point is the same in each case.*

2. *When weights of substances which are proportional to their molecular weights are dissolved in the same weight of a solvent, the lowering of the freezing point is the same in each case.*

By taking advantage of these laws it is possible to determine when two solutions contain the same number of molecules of two dissolved substances, and consequently to determine the relative molecular weights of the two substances.

Molecular weights of the elements. When we determine the weight of 22.4 l. of the various *elementary* gases, we reach some interesting conclusions. Experiment shows that the molecular weight of many of them, such as nitrogen, hydrogen, chlorine, and bromine, give values which are *twice the atomic weights*, so that in these cases the molecule contains two atoms (p. 91). In the case of the metals, so far as their vapors have been studied, the molecular weight and the atomic weight are the same, so that the molecule consists of a single atom. The molecule of ozone contains three atoms of oxygen, so that its formula is O_3, while the molecules of phosphorus and arsenic contain four atoms, giving the formulas P_4 and As_4.

Selection of atomic weights from combining weights. It is now easy to determine which multiple of the combining weight of the various elements shall be adopted as the correct atomic weight — the second problem we set out to solve in this chapter. The mode of procedure will be understood most readily by an example; so let us suppose that we have found the combining weight of nitrogen to be 7.005 and that we wish to decide whether this value or some simple multiple, 14.01 or 21.015, is the atomic weight.

We first determine the weight of 22.4 l. of a number of gaseous compounds which we know to contain nitrogen. These values are given in the first column of the table.

NAME OF GASEOUS COMPOUND	MOLECULAR WEIGHT (22.4 L.)	PERCENTAGE OF NITROGEN BY EXPERIMENT	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas . . .	27.95	100.00	27.95
Nitrous oxide . . .	44.13	63.70	28.11
Nitric oxide	30.00	46.74	14.02
Ammonia	17.05	82.28	14.03
Nitric acid	63.75	22.27	14.30

We next make a careful analysis of each of these compounds to ascertain the percentage of nitrogen present, placing the values obtained in the second column. If we multiply the molecular weight of each compound by the percentage of nitrogen, the product will be the portion of the molecular weight due to nitrogen. But since the molecules are made up of atoms, the part of a molecule due to nitrogen must represent the *sum of the weights of the nitrogen atoms present.* We notice that the numbers in the last column are either very near to 14 or to twice 14, and that none are near 7. If we examine a large number of nitrogen compounds, it is reasonable to expect that we shall find some containing only one atom, and since we find none which give a value of less than 14, we assume that this, and not 7 or 21 or 28, represents the weight of a nitrogen atom.

Accurate determination of atomic weights. The weight of a given volume of a gas is difficult to determine with great precision, and in consequence the molecular weights of gases as determined by experiment are usually subject to a very considerable error. The portion of nitrogen in 22.4 l. of the various gases is therefore a little uncertain, as will be seen from the values in the last column. All these figures tell us is that the true value is *very near* 14. The *combining weight* can be very accurately determined by the analysis of any of these compounds, and is found to be 7.005. It is therefore evident that the accurate atomic weight is twice this value; namely, 14.01.

Summary. These, then, are the steps which must be taken to establish the atomic weight of an element.

1. Determine the combining weight accurately by analysis.
2. Determine the weight of 22.4 l. of a large number of gaseous compounds of the element, and, by analysis, the part of the molecular weights due to the element. The smallest number so obtained will be the *approximate* atomic weight.

3. Multiply the combining weight by the integer (1, 2, or 3) which will give a number close to the approximate atomic weight. The number so obtained will be the *precise* atomic weight.

Equations and volumes of gases. If we have an equation which expresses a reaction in which gaseous molecules take part, we may make use of Avogadro's hypothesis to predict the volume changes which will accompany the reaction. For example, the equation

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

states that 1 gram-molecular weight of hydrogen combines with 1 gram-molecular weight of chlorine to give 2 gram-molecular weights of hydrogen chloride. Now all of these substances are gases, and a gram-molecular weight of every gas occupies the same volume; namely, 22.4 l. Consequently 1 volume of hydrogen will combine with 1 volume of chlorine to give 2 volumes of hydrogen chloride, and there will be no change in the volume due to the reaction (save as occasioned by the heat given off). *The coefficients of the molecules therefore indicate the proportion by volume in which gases take part in reactions.*

Weight of a liter of a gas. We have found that a gram-molecular weight of any gas occupies 22.4 l. If we know the molecular weight of a gas, we can at once deduce the weight of a liter of the gas. For example, the molecular weight of acetylene (C_2H_2) is 26.016. This means that 26.016 g. occupies 22.4 l. Consequently 1 l. will weigh $26.016 \div 22.4 = 1.1614$ g. In general, to find the weight of a liter of any gas, divide its molecular weight by 22.4. The value so obtained will be close enough to the experimental value for all practical purposes.

EXERCISES

1. From the following data calculate the atomic weight of sulfur. The combining weight obtained by an analysis of sulfur dioxide is 8.015. The weight of 1 l. of gas and the compositions of a number of compounds containing sulfur are as follows:

Name	Weight of 1 l.	Composition by percentage		
Hydrogen sulfide	1.5392 g.	S = 94.11	H = 5.89	
Sulfur dioxide	2.9266 g.	S = 50.05	O = 49.95	
Sulfur trioxide	3.571 g.	S = 40.05	O = 59.95	
Sulfur chloride	6.027 g.	S = 47.48	Cl = 52.52	
Sulfuryl chloride	6.030 g.	S = 23.75	Cl = 52.53	O = 23.70
Carbon disulfide	3.3928 g.	S = 84.24	C = 15.76	

2. Calculate the formulas for compounds of the following percentage compositions:

				Molecular weight
(1)	S = 39.07%	O = 58.49%	H = 2.44%	81.0
(2)	Ca = 29.40%	S = 23.56%	O = 47.04%	136.2
(3)	K = 38.67%	N = 13.88%	O = 47.45%	101.2

3. The molecular weight of ammonia is 17.06; of sulfur dioxide is 64.06; of chlorine is 70.9. From the molecular weight calculate the weight of 1 l. of each of these gases. Compare your results with the table in the Appendix.

4. What are the relative weights of the molecules of hydrogen and hydrogen chloride, as deduced from a weight of 1 l. of each of these gases?

5. Natural gas is largely composed of marsh gas (CH_4). When this burns, the equation for the reaction is as follows:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

In burning 100 cu. ft. of this gas what volume of oxygen is consumed? What is the volume of the carbon dioxide formed?

6. Why write 2 O_2 rather than 4 O in problem 5?

7. Determine the molecular weight of chloroform from the following data: In an experiment 0.2 g. of the liquid gave a volume of 42.4 cc. of gas collected over water at 20° and 740 mm.

8. The percentage composition of chloroform as determined by analysis is as follows: Cl = 89.11%; C = 10.05%; H = 0.84%. From

these figures and taking into consideration the molecular weight as determined in problem 7, calculate the formula of chloroform.

9. Solve problem 20, Chapter XXII, without using molecular weights. Compare your results.

10. When ammonia is heated to ignition in an atmosphere of oxygen it burns, forming water and liberating nitrogen. What is the relation between the volume of the ammonia burned and that of the oxygen required for its combustion? between the volume of the ammonia burned and the nitrogen liberated in its combustion?

11. Compare the volume of hydrogen sulfide with that of the oxygen required for its complete combustion.

CHAPTER XXIV

CARBON MONOXIDE; CARBONIC ACID; HYDROCARBONS

Introductory. In connection with the occurrence of carbon (p. 116), attention was called to the fact that this element is widely distributed in nature and that the number of its compounds is very large. Over 200,000 of them have been described, and many newly discovered ones are constantly being added to the list. Because the number of carbon compounds is so great and also because certain characteristics distinguish them from the compounds of other elements, it has been found convenient to group them under the general heading of *organic chemistry* and to postpone their study until the introductory course in chemistry has been concluded. Nevertheless, even an introductory course must include a limited number of the more common compounds of carbon.

THE OXIDES OF CARBON AND CARBONIC ACID

Carbon forms three oxides; namely, carbon monoxide (CO), carbon dioxide (CO_2), carbon suboxide (C_3O_2). They are all colorless gases. But little is known of the suboxide, and no further mention will be made of it. Carbon dioxide has been described in connection with carbon (p. 122).

Carbon monoxide (CO). Carbon monoxide occurs in the gases issuing from volcanoes. It can be prepared in a number of ways, the most important of which are the following:

1. *By the partial reduction of carbon dioxide.* When carbon dioxide is conducted over highly heated carbon the monoxide results:

$$CO_2 + C \longrightarrow 2\,CO$$

When coal burns in a stove carbon dioxide is at first formed in the free supply of air, but as the hot gas rises through the glowing coals it is reduced to carbon monoxide. When this gas comes in contact with the air above the coal, the gas combines with oxygen to form carbon dioxide, burning with the blue flame so often noticed above a bed of coals, especially in the case of hard coal.

2. *By the decomposition of formic acid.* In the laboratory carbon monoxide is usually prepared by heating formic acid (CH_2O_2) or its sodium salt with sulfuric acid:

$$CH_2O_2 \longrightarrow H_2O + CO$$

The sulfuric acid assists in the reaction by combining with the water formed. The carbon monoxide may be collected over water, since it is but slightly soluble.

Oxalic acid ($C_2H_2O_4$) may be used in place of formic acid:

$$C_2H_2O_4 \longrightarrow CO + CO_2 + H_2O$$

In this case, however, it is necessary to pass the gaseous mixture through a solution of sodium hydroxide to remove the carbon dioxide.

Properties. Carbon monoxide is a colorless and odorless gas. It is 0.967 times as heavy as air and is very difficult to liquefy. It burns in air or in oxygen with a blue flame, forming carbon dioxide. It combines with chlorine to form the colorless gas $COCl_2$, known as *phosgene*, or *carbonyl chloride* — a compound used in very large quantities in the World War as a poison gas. Carbon monoxide also combines directly with some of the metals, as nickel and iron. Because of its affinity for oxygen it is a good reducing agent, as shown in the following equation:

$$CuO + CO \longrightarrow Cu + CO_2.$$

Carbon monoxide is very poisonous, and being nearly odorless, it is a very treacherous poison. Deaths not infrequently result from the stoppage of stovepipes or chimneys. The draft of air is diminished to such an extent that carbon monoxide rather than dioxide is the main product of combustion and, not having egress through the chimney, escapes into the room. It is an interesting fact that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril.

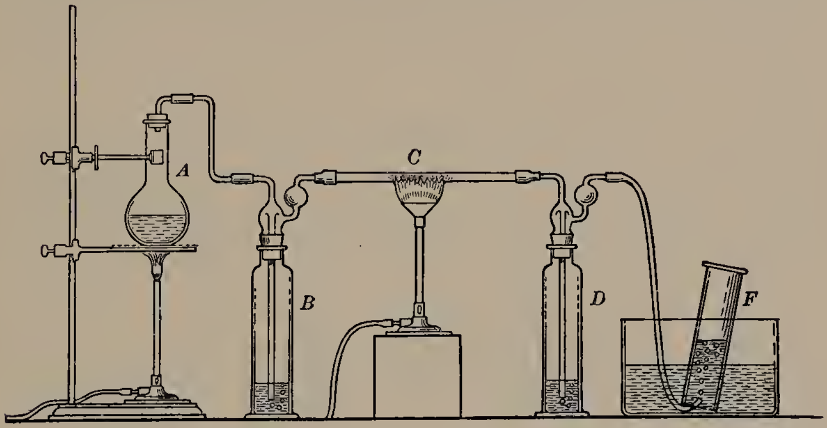


FIG. 110. The reducing power of carbon monoxide, as shown in the reduction of copper oxide by the hot gas

The reducing power of carbon monoxide. Fig. 110 illustrates a method of showing the reducing power of carbon monoxide. The gas is generated by gently heating a mixture of formic acid and sulfuric acid in the flask *A*. The bottle *B* contains a little water to wash the gas. *C* is a hard-glass tube containing copper oxide, which is heated by a burner. The black copper oxide is reduced to reddish metallic copper by the carbon monoxide, which is in turn changed to carbon dioxide. The formation of the carbon dioxide is shown by the precipitate in the calcium hydroxide solution in *D*. Any unchanged carbon monoxide is collected over water in *F*. If oxalic acid is used in preparing the oxide, bottle *B* should contain a solution of sodium hydroxide to remove the carbon dioxide which is formed along with the monoxide.

Carbonic acid (H_2CO_3). Like most of the oxides of the nonmetallic elements, carbon dioxide is an acid anhydride. It combines with water to form an acid of the formula H_2CO_3, called carbonic acid:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

The acid is, however, very unstable and cannot be isolated. Only a very small amount of it is actually formed when carbon dioxide is passed into water, as is evident from the small solubility of the gas. If, however, a base is present in the water, salts of carbonic acid are formed, and these are quite stable:

$$2\,NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2\,H_2O$$

Action of carbon dioxide on bases. This conduct is explained by the principles of reversible reactions. The equation

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

is reversible, and the extent to which the reaction progresses depends upon the relative concentrations of each of the three factors in it. Equilibrium is ordinarily reached when very little H_2CO_3 is formed. If a base is present in the water to combine with the H_2CO_3 as fast as it is formed, all of the CO_2 is converted into H_2CO_3 and thence into a carbonate.

Salts of carbonic acid; carbonates. The carbonates form an important class of salts. Limestone, shells, and marble are largely calcium carbonate ($CaCO_3$), common washing soda is sodium carbonate (Na_2CO_3), and baking soda is sodium acid carbonate ($NaHCO_3$). The carbonates of sodium, potassium, and ammonium only are soluble, and these can be made by the action of carbon dioxide on solutions of the bases, as has just been explained.

The insoluble carbonates are formed as precipitates when soluble salts are treated with a solution of a soluble carbonate. Thus, the insoluble calcium carbonate can be made by bringing together solutions of calcium chloride and sodium carbonate, as follows:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCl$$

Most of the carbonates are decomposed by heat, yielding carbon dioxide and an oxide of the metal. Thus, calcium oxide (lime) is made by heating calcium carbonate (limestone), as follows:

$$CaCO_3 \longrightarrow CaO + CO_2$$

The carbonates are readily acted upon by acids, liberating carbon dioxide (p. 123).

Action of carbon dioxide on calcium hydroxide. If carbon dioxide is passed into a solution of calcium hydroxide (limewater), calcium carbonate is at first precipitated (p. 125):

$$H_2O + CO_2 \longrightarrow H_2CO_3,$$
$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2\,H_2O$$

If the current of carbon dioxide is continued, the precipitate soon dissolves because the excess of carbonic acid forms calcium acid carbonate, which is soluble:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

If now the solution is heated, the acid carbonate is decomposed and calcium carbonate once more precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2CO_3$$

Cyanogen (C_2N_2) and hydrogen cyanide (HCN). At high temperatures carbon unites with nitrogen to form the colorless, very poisonous gas, cyanogen (C_2N_2). With hydrogen and nitrogen it forms hydrogen cyanide (HCN). This is a colorless liquid boiling at 26°. It has a peculiar odor suggesting peach kernels and is *extremely poisonous* either when its vapor is inhaled or when the liquid is taken internally. The vapor is often used to destroy insects. It is soluble in water in all proportions, forming the solution known as *hydrocyanic acid* or, more frequently, as *prussic acid.* It is a very weak acid. Its salts are called cyanides and, like the acid itself, are very poisonous. Sodium cyanide (NaCN) and potassium cyanide (KCN) are white solids. Their solutions readily dissolve gold and are often used for extracting gold from its ores.

Since hydrogen cyanide is very volatile, it is easily liberated from the cyanides by the action of sulfuric acid (p. 225), and this is the usual method for preparing it:

$$KCN + H_2SO_4 \longrightarrow HCN + KHSO_4$$

Structural formula of hydrogen cyanide. In some reactions hydrogen cyanide acts as though it had the formula $H{-}C{\equiv}N$, while other reactions indicate the formula $H{-}N{=}C$. These facts can be explained by the assumption that what we know as hydrogen cyanide is really a mixture of two compounds in equilibrium with each other as indicated in the following equation:

$$HCN \rightleftarrows HNC$$

The hydrocarbons. Carbon and hydrogen unite to form a great many compounds. These are known collectively as the *hydrocarbons.* Their importance may be inferred from the fact that, mixed in varying proportions, they constitute such valuable substances as natural gas, gasoline, kerosene, vaseline, and paraffin; moreover, from them are prepared most of our dyes and some of our most powerful explosives.

Classes of hydrocarbons. In order to simplify the study of the hydrocarbons, it is convenient to arrange them in groups, or *series*. The most important of these are the *methane* series and the *benzene* series.

1. ***The methane series of hydrocarbons.*** In the following table are given the names, formulas, and boiling points of some of the members of the methane series:

NAME AND FORMULA	BOILING POINT	NAME AND FORMULA	BOILING POINT
Methane (CH_4) . . .	– 160°	Pentane (C_5H_{12}) . . .	+ 36°
Ethane (C_2H_6) . . .	– 93°	Hexane (C_6H_{14}) . . .	+ 69°
Propane (C_3H_8) . . .	– 45°	Heptane (C_7H_{16}) . . .	+ 98°
Butane (C_4H_{10}) . . .	+ 1°	General formula (C_nH_{2n+2})	

Each member of this series differs from the one preceding it by the group of atoms (CH_2), and the boiling points gradually increase. All the members of this series are known up to the one having the formula $C_{28}H_{58}$. The lower members are gases, the intermediate members are liquids, and the higher members are solids. They are all combustible.

The great source of the methane hydrocarbons is petroleum, an oil obtained by boring deep wells into the earth in certain localities (Fig. 111). This oil is composed principally of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons.

2. ***The benzene series of hydrocarbons.*** The most important members of the benzene series are benzene (C_6H_6) and toluene (C_7H_8). Both are colorless liquids, the former boiling at 80.2° and the latter at 110°. The benzene hydrocarbons are obtained from coal tar, a sticky black

liquid obtained in the manufacture of coke and coal gas. They are of great importance in the manufacture of dyes and explosives.

Production and refining of petroleum. The chief oil-producing regions in the United States are in California, Oklahoma, Illinois, and Texas. The United States produces annually about 300,000,000 barrels, which is about two thirds of the world's output. The oil is pumped to the surface and stored in large tanks (Fig. 111) until refined.

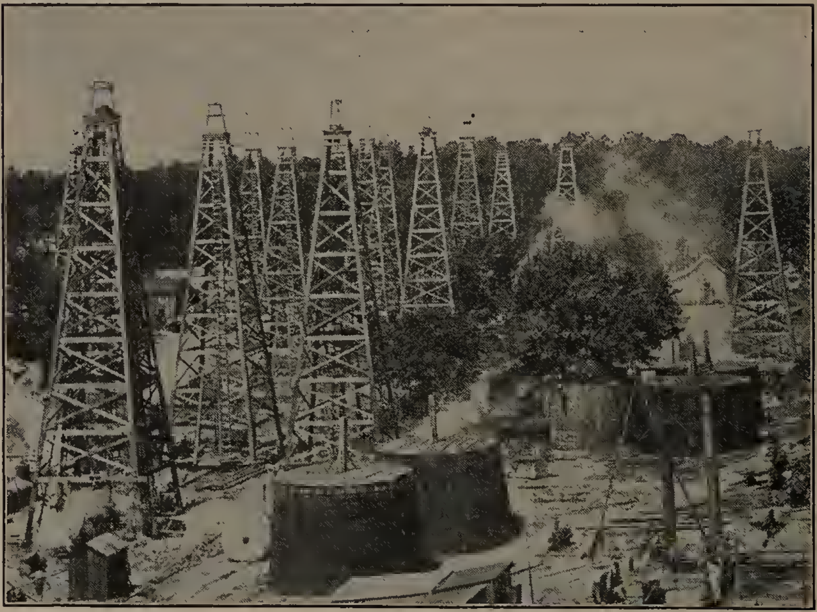


FIG. 111. Typical scene in an oil field, showing the wells and the storage tanks

Petroleum, except when the crude product is used as a fuel, is always subjected to a refining process in which the oil is separated into different constituents which are then purified. In this process the crude oil is run into large iron stills (Fig. 112) and subjected to distillation.

The distillates which pass over between certain limits of temperature are kept separate from each other and serve for different purposes. Thus, the liquid distilling between approximately 70° and 150° is known as naphtha, that distilling between 150° and 300° is ordinary kerosene (coal oil), while the oils passing over above 300° are used as lubricating oils. The oils that are semisolid at ordinary temperature constitute vaseline. The liquid remaining after the higher-boiling oils have distilled over is chilled, whereupon the solid constituents dissolved in the oil separate. These are filtered off and yield such products as paraffin and ceresin.

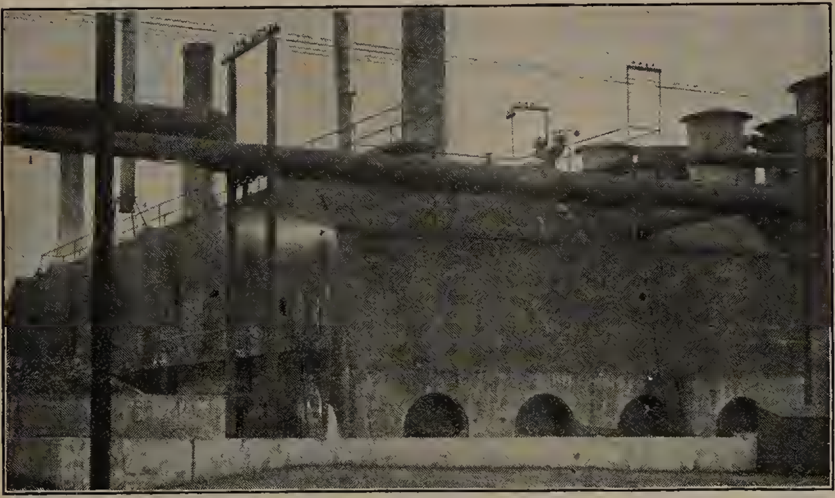


Fig. 112. Stills for refining petroleum

The naphthas. A number of different naphthas are recognized commercially, differing in boiling points and densities. Those of low boiling point are called *gasoline* and are used in gasoline engines and as a fuel; those of a higher boiling point are used in making paints. *Benzine* is a high-boiling naphtha, and being a good solvent for such organic substances as fats and oils, is used in cleaning fabrics (dry-cleaning).

The various products obtained from petroleum by distillation are purified, usually by washing first with sulfuric acid, then with sodium hydroxide, and finally with water.

It is evident from the method of preparation that the products obtained from petroleum such as gasoline and kerosene are not definite hydrocarbons but mixtures of hydrocarbons that boil between certain limits of temperature. (One should not confuse the two products, *benzene* and *benzine*: the former is a definite hydrocarbon, C_6H_6, obtained chiefly from coal tar, while the latter is a mixture of low-boiling hydrocarbons obtained from petroleum.)

Because of the ease with which benzine burns, as well as of the explosive character of a mixture of its vapor and air, many accidents result from its use, especially when it is employed in our homes for cleaning fabrics. The greatest care must be taken in cleaning silk, since friction often causes a spark.

The cracking of oils. Formerly kerosene was the most important of the products obtained from petroleum. At present, however, gasoline is by far the most valuable, so that every effort is now made to increase the yield of gasoline. To accomplish this the distillation is carried on under conditions that tend to decompose the heavier molecules making up the higher-boiling liquids into the simpler molecules which constitute liquids of lower boiling points. The process is known as the *cracking* of oils. It consists essentially in vaporizing the oils and then heating the vapor under considerable pressure. Good results are obtained at a temperature of from 500° to 550° and under a pressure of 12 atmospheres. It is of great interest to note that it is possible in this way not only greatly to increase the yield of gasoline obtainable from a given sample of petroleum but also by selecting proper conditions of temperature and pressure, to bring about reactions that result in the formation of certain hydrocarbons of the benzene series, especially benzene and toluene. This method is being used to some extent in the preparation of benzene and toluene, since both of these compounds are very valuable for the preparation of dyes and explosives.

Methane (marsh gas) (CH_4). Methane is the first member of the methane series of hydrocarbons (p. 297). It constitutes from 90 to 95 per cent of natural gas. It is formed in marshes by the decay of vegetable matter under water, and bubbles of the gas are often seen to rise when the dead leaves on the bottom of pools are stirred. It also collects in mines, and, when mixed with air, is called *fire damp* by the miners, because of its great inflammability, *damp* being an old name for *gas*. It is formed when organic matter, such as coal or wood, is heated in closed vessels, and is therefore a principal constituent of coal gas. Pure methane is a colorless, odorless gas about one half as heavy as air. It is but slightly soluble in water. When ignited it burns with a pale-blue flame:

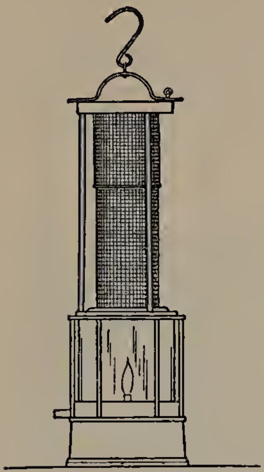


FIG. 113. The miner's safety lamp

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 213{,}500 \text{ cal.}$$

Safety lamp. Fortunately the kindling temperature of fire damp is high, and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (Fig. 80) invented a miner's lamp based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 113). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases and the explosion is confined to the interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen flame and parallel with the table (Fig. 114).

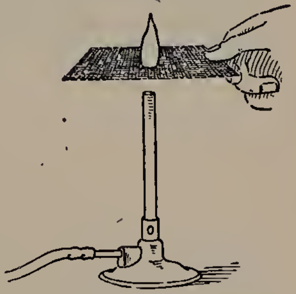


FIG. 114. An experiment to illustrate the principle of the safety lamp

When the gas is turned on and a light applied above the gauze, the resulting flame rests upon the gauze, but does not pass through it to the burner.

Halogen derivatives of methane. As a rule the hydrogen present in a hydrocarbon may be displaced by a halogen element, atom for atom. In this way there are formed from methane a number of derivatives, the most important of which are the following:

Chloroform ($CHCl_3$), a heavy colorless liquid boiling at 61°, is the well-known anesthetic used in surgery. *Carbon tetrachloride* (CCl_4) resembles chloroform in appearance. It is a good solvent, especially for fatty substances. It is often used to remove grease spots from fabrics, and is sold for this purpose under the name of *carbona*. It possesses the advantage over benzine of being noninflammable, but is more expensive. *Iodoform* (CHI_3) is a yellow crystalline solid and is largely used as an antiseptic in the treatment of wounds.

Acetylene (C_2H_2). This hydrocarbon is a colorless gas and is now made in large quantities by the action of water on calcium carbide (CaC_2):

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

The gas when pure has a faint, pleasant odor, the disagreeable odor of ordinary acetylene being due to impurities. It is an endothermic compound; that is, it decomposes with evolution of heat:

$$C_2H_2 \longrightarrow 2\,C + H_2 + 49{,}300 \text{ cal.}$$

Acetylene, with the proper admixture of air, burns with a brilliant white light. The flame is very hot because to the heat of combustion of the carbon and hydrogen present there is added the heat of decomposition of the acetylene undergoing combustion:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2 \times 301{,}630 \text{ cal.}$$

Acetylene is very explosive when subjected to pressure. It has been found that the gas can be compressed with safety, however, by forcing it at low temperatures into metal cylinders completely filled with some porous material such as a mixture of asbestos and cotton, which has been partially saturated with certain liquids (acetone, a liquid obtained by the destructive distillation of wood, is often used). These liquids absorb large volumes of the gas, and under such conditions it is not explosive. Stored in this way the gas is now a common article of commerce.

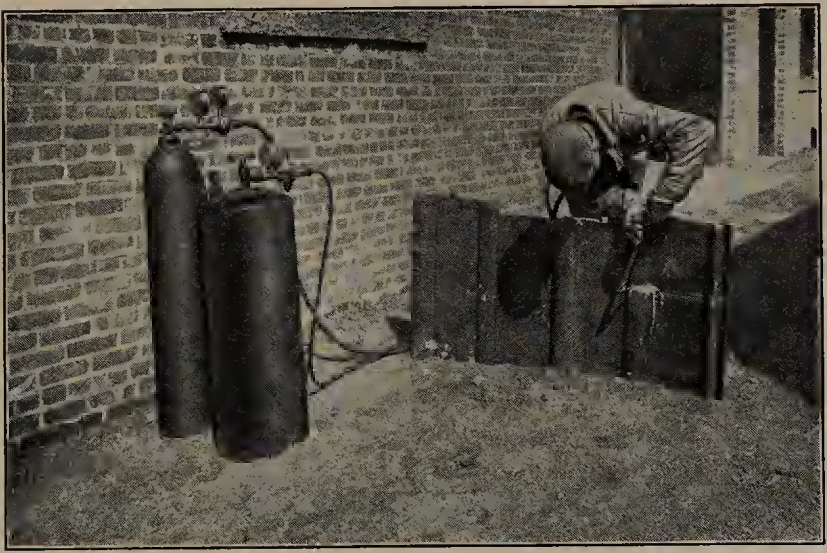


FIG. 115. Cutting an iron plate by means of the oxyacetylene blowpipe

Uses of acetylene. As an illuminant, acetylene is often used in places where electric lights are not available. The chief use of the gas at present is in the cutting and welding of metals and in burning out the carbon deposited in the cylinders of gasoline engines. For these purposes acetylene is burned in pure oxygen in a form of apparatus known as the *oxyacetylene blowpipe*, which is almost exactly like the oxyhydrogen blowpipe. A temperature of about 2700° may be obtained in this way. This blowpipe has been found especially useful in dismantling iron structures, since the tip of the flame, when drawn slowly over the metal, burns it at the point of contact (Fig. 115) and so cuts the metal into pieces.

EXERCISES

1. Determine the percentage composition of carbon monoxide and carbon dioxide; of marsh gas and acetylene.

2. How could you prove that carbonic acid is formed when carbon dioxide is passed into water? What other gases have we studied that combine with water?

3. Why do most acids decompose carbonates?

4. What compound would be formed by passing carbon dioxide into a solution of potassium hydroxide? Write the equation.

5. Suggest a method for the preparation of ammonium carbonate.

6. In what respect are carbonic acid and sulfurous acid similar?

7. How could you distinguish between sodium carbonate (Na_2CO_3) and sodium sulfite (Na_2SO_3)?

8. Give the reasons why the reaction which takes place when calcium acid carbonate is heated completes itself.

9. Could a solution of sodium hydroxide be substituted for the solution of calcium hydroxide in testing for carbon dioxide?

10. How could you distinguish between gasoline and kerosene?

11. Could asbestos fibers be used to replace the wire in a safety lamp?

12. What weight of formic acid is necessary for the preparation of 10 l. of carbon monoxide?

13. (*a*) What volume of oxygen is required for combustion of 10 l. of carbon monoxide? (*b*) What is the volume of the carbon dioxide formed?

14. What volume of oxygen would be required to burn 10 l. of methane? of acetylene? What volume of carbon dioxide would be formed in each case?

15. What weight of formic acid would be required in the preparation of sufficient carbon monoxide to reduce 10 g. of copper oxide to copper?

16. What weight of sodium hydroxide is necessary to neutralize the carbonic acid formed by the action of hydrochloric acid on 100 g. of calcium carbonate?

17. On the supposition that calcium carbide costs 12 cents a kilogram, what would be the cost of an amount sufficient to generate 100 l. of acetylene measured at 20° and 740 mm.?

18. (*a*) How many calories of heat are evolved in the combustion of 100 l. of acetylene? (*b*) What weight of water at 20° would this heat convert into steam at 100°?

19. Supposing that gasoline is pure heptane, what volume of air is necessary to burn 1 kg. of the liquid? What volume of carbon dioxide would be formed?

CHAPTER XXV

FUELS; FLAMES; ELECTRIC FURNACES

Fuels. Many substances are used as sources of heat, the most important being the various fuel gases, together with coal, wood, and petroleum. The composition of several of these fuel gases is given in the table on page 311. Most of them serve as illuminants as well as for fuels.

Coal gas. It has been known for several centuries that when soft, or bituminous, coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was used for street lighting in London and Paris more than a hundred years ago.

The manufacture of coal gas. The manufacture of coal gas is represented in a diagrammatic way in Fig. 116. The coal is introduced into a closed retort *A* and heated by the fire below. A number of these retorts are placed in horizontal rows, each being furnished with a delivery pipe. This delivery pipe leads into a large pipe *B* (known as the *hydraulic main*) which runs at right angles to the retort. The application of heat causes the coal to undergo complex changes which result in the formation of a large number of compounds. These compounds escape through the delivery pipe into the hydraulic main. From the hydraulic main the impure gas then passes into a series of pipes *C*, in which it is cooled. Here is deposited a thick, tarry mass known as *coal tar*, which is a mixture of a large number of liquid and solid products formed in the heating of the coal. On the top of the tar there collects a liquid, mostly water, containing ammonia and known as the *ammoniacal liquor*. In the scrubber *D* the gas passes through a column of loose coke, over which water is sprayed, where it is still further cooled and to some extent purified from soluble gases, such as hydrogen sulfide and ammonia. In the purifier *E* it passes over a bed of lime or of iron oxide, which removes the remainder of the sulfur compounds, and from this it enters the large gas holder *F*, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor.

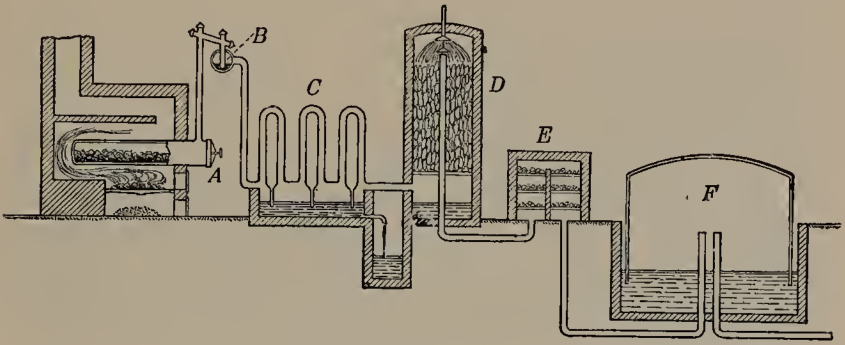


FIG. 116. Diagram of a plant used for the manufacture of coal gas and its by-products

Not only is the ammonia obtained in the manufacture of the gas of great importance (p. 205) but the coal tar is the source of many very useful substances; for example, most dyes, as well as most of the explosives used in war, are prepared from compounds derived from coal tar. This subject will be discussed in a later chapter.

The by-product coke oven. It will be observed that coke is formed in the process used in the manufacture of coal gas. Coke is a very important product and is used in large quantities, especially in the reduction of metals, such as iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. The additional coke required has been prepared for the most part by coking the coal in ovens called beehive ovens because of their shape. The coking of coal in these ovens is carried out as follows: The oven is nearly filled with coal and the coal is ignited. After the fire is well started the draft is shut off, and the heat formed in the combustion of a portion of the coal is sufficient to coke the remainder of the coal. In this process all the coal tar, coal gas, and ammonia escape through an opening in the top of the furnace and are lost. The growing demand for ammonia, as well as for the products obtained from coal tar, has led to the construction of furnaces or ovens for the coking of coal which make it possible to save the coal tar and ammonia formed in the process. Such ovens are known as *by-product coke ovens*, this term being chosen because the ammonia and coal tar formed in the process of coking the coal are by-products, the coke being the main product. These ovens are very much more complex than the beehive ovens, but the demand for ammonia and coal tar is rapidly becoming so great as to cause the gradual introduction of the by-product ovens, although most of our coke is still made in the beehive ovens.

Fig. 117 represents a large by-product coking plant. The ovens *A* are placed side by side in an upright position. The coal is carried up through the shaft *B* and introduced into the ovens from above. The coal tar collects in the large main *C*. The more volatile portions which escape condensation in *C* are condensed in appropriate pipes. A portion of the coal gas generated in the process is used as fuel for coking the coal.

Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is manufactured by passing superheated steam over very hot anthracite coal or coke, the chief reactions being expressed in the following equations:

$$C + H_2O \longrightarrow CO + H_2 - 26{,}990 \text{ cal.}$$
$$CO_2 + C \longrightarrow 2\,CO - 37{,}230 \text{ cal.}$$

The industrial process is intermittent. The fuel is burned with a forced draft in a suitable furnace until it is very hot.

The air is then shut off and the steam turned on until the temperature falls to about 1000°. The process is then reversed. The fall in temperature is rapid, partly owing to radiation and to the cooling occasioned by the steam, but largely because of the endothermic character of the reactions which take place. The gas so formed contains all the nitrogen which was in the furnace when the steam was admitted.

Water gas burns with a pale-blue nonluminous flame. It is very poisonous and has no odor. To make it suitable for illumination in an ordinary burner, as well as to give it an odor and so make it safer, it must be enriched with hydrocarbons called illuminants. This is accomplished by passing the gas through a furnace filled with hot fire brick upon which crude petroleum is sprayed. The petroleum oils are decomposed (cracked) into simpler gaseous bodies, the most important of which are methane, acetylene, and ethylene. Coal gas is sometimes enriched in a similar way by adding petroleum to the coal in the retorts.

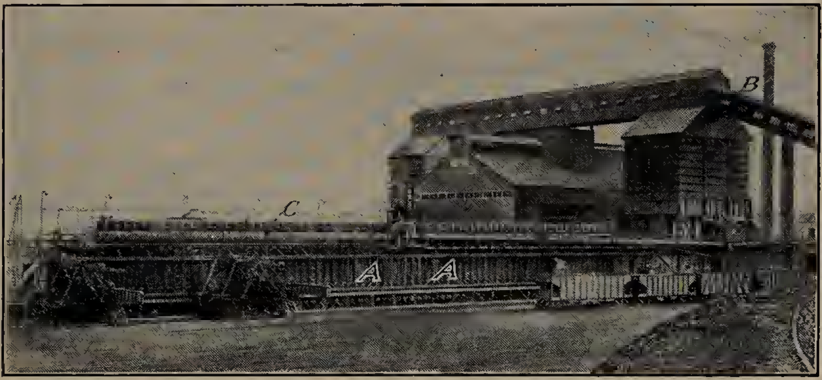


Fig. 117. A modern by-product coke oven

Producer gas. Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal under such conditions that the product of combustion is largely carbon monoxide (Fig. 118). Very often a little steam is admitted with the air, and this on passing through the hot bed of coals is reduced as in the preparation of water gas. Made in this way, producer gas is composed mainly of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality, even from lignite, and as gas engines run well with this gas, it furnishes the most economical method for utilizing low-grade coal for power.

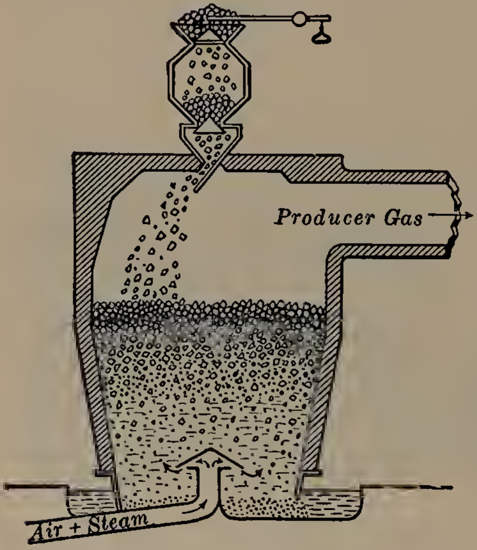


FIG. 118. Diagram of the method of making producer gas

Natural gas. In many regions of the United States, as well as in other countries, natural gas is obtained from wells drilled into a stratum holding the gas. While it is variable in composition, it consists largely of methane, many samples containing as much as 95 per cent of this compound. It burns with a flame of moderate luminosity, but works well with a gas mantle. It has a high heat of combustion, as shown in the following equation:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 213{,}500 \text{ cal.}$$

It is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities.

Comparative composition of gases. The following figures are the results of analyses of average samples, but since each kind of gas varies considerably in composition, the values are to be taken as approximate only. The nitrogen and traces of oxygen are derived from the air.

COMPOSITION OF GASES EXPRESSED IN PERCENTAGE BY VOLUME

Formula of the constituent gases	Ohio natural gas	Coal gas	Water gas	Enriched water gas	Producer gas
H_2		41.3	52.88	37.96	10.90
CH_4	89.5	43.6	2.16	7.09	
C_6H_6	9.3			2.01	
$C_2H_2 + C_2H_4$ . .	0.3	3.9		9.40	0.60
CO	0.4	6.4	36.80	32.25	20.10
CO_2	0.3	2.0	3.47	4.73	8.50
N_2	0.2	1.2	4.69	3.96	59.90
O_2		0.3		0.60	
Other hydrocarbons		1.5		1.80	

Relation of the two gases to the flame. The gas issuing from the burner is said to undergo combustion, while that one which constitutes the atmosphere about the flame is said to support combustion. These terms are entirely conventional, since the relation of the two gases may be reversed without greatly altering the appearance of the flame.

Fig. 119 illustrates a convenient apparatus for demonstrating this fact. A wide lamp chimney (*A*) is covered with a piece of asbestos board (*B*) which has a hole in the center about as large as a dime. A straight tube (*C*) about 1 cm. wide and also a smaller tube (*D*) connected with the gas supply

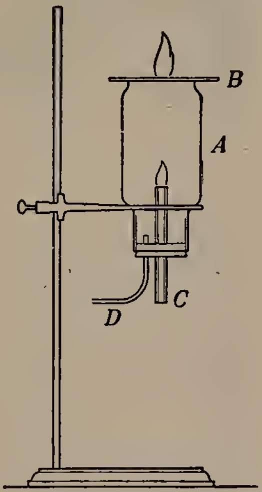


Fig. 119. Apparatus for showing the relation of two gases to the flame produced by their union

pass through a cork at the bottom. If the hole in *B* is closed (by a piece of asbestos board) while gas is admitted through *D*, the excess gas escapes downward through *C*, where it may be lighted. If the hole in *B* is now opened, the flame will ascend to the top of the tube *C*. This flame is produced by air drawn up through *C*, burning in an atmosphere of coal gas. Finally, the excess of coal gas may be ignited at *B*, where it will burn in air, the two flames being very similar in their appearance.

Fig. 120. Materials used in making gas mantles, and stages in the process of manufacture

Gas mantles. In using the fuel gases as illuminants the gas is usually mixed with air before burning. In this way the gas burns with a hot but nearly nonluminous flame. The light is obtained by suspending about this flame a gauze mantle of suitable material. The best mantles are composed of a mixture of 99 per cent of thorium oxide with 1 per cent of cerium oxide.

The thorium and cerium compounds used in gas mantles are obtained from *monazite sand* (Fig. 120) found principally in North Carolina and Brazil. The process of making a gas mantle consists in knitting a tubular fabric, which is then dipped into a solution of the nitrates of thorium and cerium. After being dried the fabric is heated, in which process the yarn is burned, while the nitrates of thorium and cerium are converted into oxides which are left in the form of the original fabric. The resulting mantle is very delicate and is strengthened for shipping by dipping it into a solution of an appropriate substance and drying.

Products of the combustion of ordinary fuels. Ordinary fuels, such as oil, wood, coal, and fuel gases, are largely made up of carbon and hydrogen or their compounds. The chief products of the combustion of such fuels are carbon dioxide and water. Associated with these are small amounts of other products, such as carbon monoxide and sulfur dioxide, the later being formed from traces of sulfur compounds in the fuels.

Rooms are not infrequently heated by gas or oil stoves, with no provisions for removing the products of combustion. Likewise, natural gas is often burned in stoves or grates with the damper closed so as to leave no opening into the chimney. Such practices are greatly to be condemned, since the air in the rooms heated in this way soon becomes so contaminated with the various products of combustion as to render it unfit for respiration. The large amount of water vapor formed in rooms so heated condenses on the windows in cold weather, causing the glass to *sweat.*

Conditions necessary for flames. When one of the substances undergoing combustion remains solid at the temperature occasioned by the combustion, light may be given off, but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, but no flame is seen.

When, however, both of the substances involved are gases or vapors at the temperature reached in the combustion, the act of union is accompanied by a *flame.*

Flames from burning liquids or solids. Many substances which are liquids or solids at ordinary temperatures burn with a flame because the heat of combustion slowly vaporizes them, and the flame is due to the union of this vapor with the oxygen of the air. This may be shown in the case of a candle flame by holding one end of a slender glass tube in the base of the flame (Fig. 121). The unburned vapor in the inner part of the flame is thus conducted away, and may be ignited at the upper end of the tube.

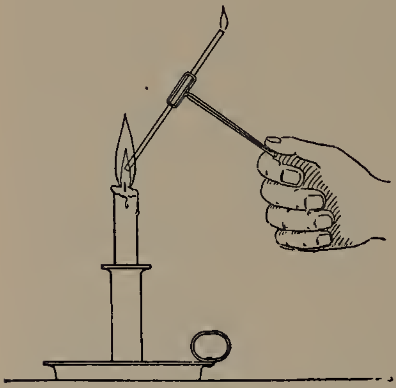


Fig. 121. An experiment to show that the interior of a candle flame contains combustible gases

Bunsen burners. In the ordinary Bunsen burner, and in similar burners used in gas ranges and for illumination with the aid of mantles, the gas is mixed with a certain percentage of air before it is burned. This is accomplished by having an opening (mixer) in the base of the burner into which the air is drawn by the flow of the gas. If the mixer is adjusted so that the proper amount of air is admitted, the flame is colorless. Such a flame possesses an advantage in that it is very hot and no carbon is deposited from it.

Structure of a flame. The structure of a flame can be studied to the best advantage when the combustible gas issues from a round tube into an atmosphere of the gas supporting combustion (usually the air), as is the case with an ordinary Bunsen burner (Fig. 122). Under these conditions the flame is conical in outline.

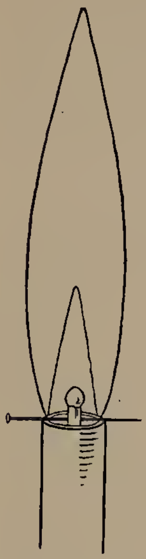


FIG. 122. A simple Bunsen flame

Simple flames. When the chemical action taking place in the combustion is the mere union of two gases, as is true in the union of hydrogen or carbon monoxide with oxygen or of hydrogen with chlorine, the structure of the flame is very simple. It consists of two superimposed cones of different altitudes. The inner one may be shown to be merely unchanged cold gas, and is therefore not a real part of the flame. A match head suspended in this region (Fig. 122) before lighting the gas is not ignited by the flame around it.

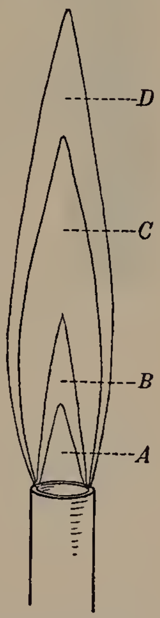


FIG. 123. The cones of a complex flame

Complex flames. In the burning of hydrocarbons, as well as of many other gases, the flame is more complex, and as many as four distinct cones may be seen (Fig. 123). The innermost one (*A*) is really not a part of the flame, being formed of gas not yet brought to the point of combustion. If a Bunsen burner is employed, with the ring at the base turned to admit plenty of air, the second cone (*B*) is sharply defined and is bluish green in color. If the burner tube is wide or too much air is admitted, the rate of combustion in this cone may exceed the rate of flow of the gas, in which case cone *A* will disappear and the flame will travel down the tube and burn at the base, or *strike back*. As the air is shut off it will be seen that a luminous spot appears at the apex of cone *B*, which gradually takes the form of a cone (*C*) quite covering the inner one and brightly luminous over all its surface. Finally, if some object is held so as to intercept the light from this region, it will be seen that there is a fourth cone (*D*), which is only faintly luminous.

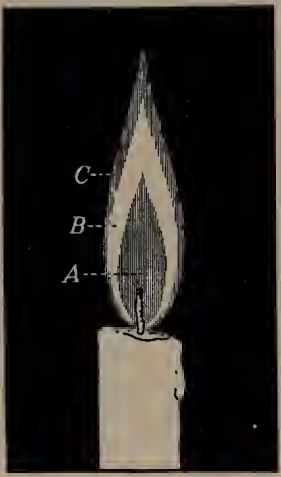


FIG. 124. The cones of a candle flame

In the candle flame (Fig. 124) there are, broadly speaking, three cones: (1) the inner cone (*A*), composed of combustible vapors; (2) an intermediate cone (*B*), in which these vapors are decomposed by the heat and carbon is set free, which renders the flame luminous; and (3) an almost invisible narrow outer cone, or film (*C*), in which the carbon and hydrogen are burned to water and carbon dioxide.

Luminosity of flames. As the cold gas in the inner cone moves toward the hottest region of the flame, its temperature rapidly rises, and at definite temperatures, which depend upon the nature of the gas, decomposition takes place. These decompositions cause sharp changes in the density of the gas, and this in turn makes the gas visible, just as air, heated by a hot pavement in summer, is visible in wavering lines. In this decomposition, products may be formed that are solids (such as carbon), and these become incandescent at the temperature reached, making the flame still more luminous. Each chemical change really produces a distinct cone in a steady flame. The luminosity of a flame thus depends upon many factors.

The following equations show some of the successive reactions that may take place in the combustion of three different gases:

$$CH_4 \longrightarrow C+2H_2 \longrightarrow C+2H_2O \longrightarrow CO_2+2H_2O$$
$$H_2S \longrightarrow S+H_2 \longrightarrow S+H_2O \longrightarrow SO_2+H_2O$$
$$2H_3As \longrightarrow 2As+3H_2 \longrightarrow 2As+3H_2O \longrightarrow As_2O_3+3H_2O$$

If we have a flame from any one of these burning gases and suddenly place a cold object (a small porcelain dish) in the flame, the free element is chilled below its kindling temperature and is deposited as soot (carbon, sulfur, arsenic) upon the dish.

The temperature of flames. The actual temperature which can be realized in an ordinary flame obviously depends upon many conditions, such as the composition of the gas, its pressure, temperature, and rate of flow, and the method of supplying the air. Even in an ordinary Bunsen flame burning under favorable conditions it is very difficult to determine the maximum temperature attained. The actual region of great heat is limited, as the burning zones are very thin. The temperature in different parts of the flame varies greatly, and any object placed in the flame for determining its temperature cuts across many different regions and is unequally heated. Evidently the temperature is much higher than that recorded by a body in the flame, since the specific heat of solids is so much greater than that of gases. Under exceptional conditions it has been found

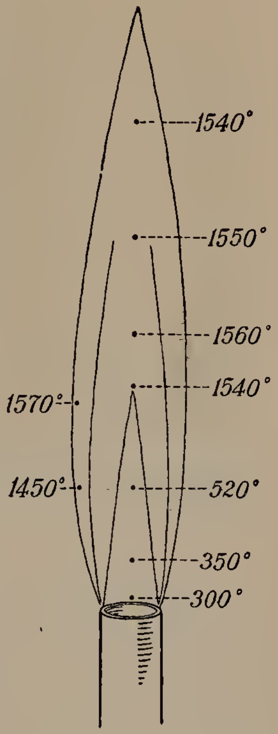


Fig. 125. An estimate of the temperature in various parts of a Bunsen flame

possible to melt a very fine platinum wire in a good Bunsen flame, so that a temperature of 1755° is surely reached. The accompanying diagram (Fig. 125) gives a rough estimate of the probable temperature in various parts of a good nonluminous Bunsen flame.

Reducing and oxidizing flames. Since the region just below the luminous cone is very hot and contains the reducing gases hydrogen and carbon monoxide, a substance such as a metallic oxide placed in this region will undergo reduction, provided it can be reduced by such hot gases. A body heated in this way is said to be heated in the *reducing flame*. At the apex of the flame there are no reducing gases, but it is very hot and air is abundant; consequently a substance which is rather readily oxidized will undergo oxidation if heated in this region. This part of the flame is called the *oxidizing flame*.

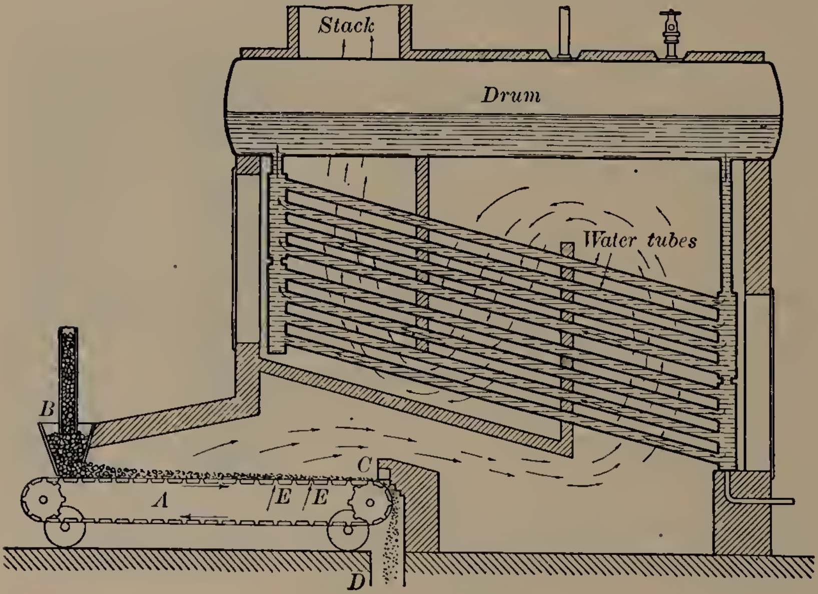


Fig. 126. Diagram of a smoke-consuming furnace

Smoke prevention. Since the products of combustion of fuels are carbon dioxide and water vapor and these are invisible compounds, it is evident that if the combustion is complete no smoke will be formed. As a rule the combustion is imperfect; gaseous compounds containing carbon are first formed, and when these are imperfectly burned a part of their carbon is set free in a finely divided state constituting smoke. Smoke may therefore be prevented by securing the complete combustion of the fuel, the necessary conditions being as follows: (1) a sufficient supply of air; (2) thorough mixing of the air with the combustible gases produced from the fuel; and (3) a temperature high enough to maintain active combustion.

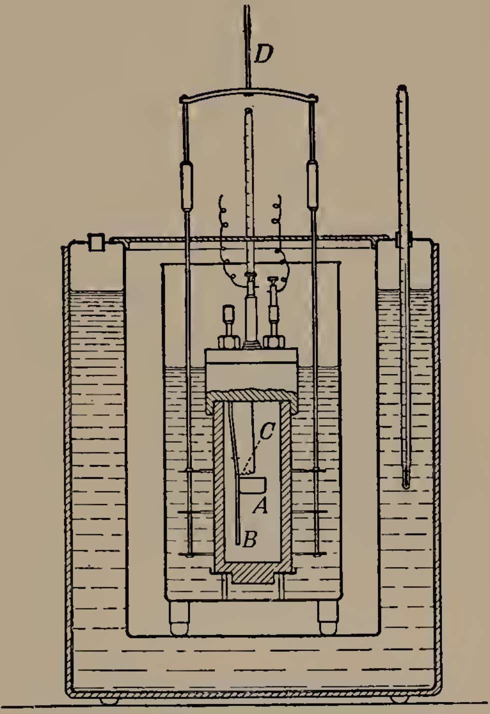


Fig. 127. A bomb calorimeter

Smoke prevention is a problem of great economic importance, especially in the large cities. Thus, for example, it has been estimated that the smoke in the city of Pittsburgh costs the people of the city $10,000,000 yearly, or about $20 for each inhabitant; and this does not take into account the possible effect of smoke upon health. Because of these facts many cities are now taking steps to abate the smoke nuisance. That the conditions necessary for preventing smoke may be met, it is essential that the coal be introduced into the furnace uniformly, so that the volatile matter expelled upon heating may be more readily mixed with air. This is done efficiently by having a chain grate, as is shown in *A* (Fig. 126). The coal is fed on this at *B*, and as the chain slowly moves forward, the coal gradually enters the furnace, and by the time it reaches the back part of the furnace (*C*) it is completely burned, the ashes falling out at *D*. The volatile matter expelled is thoroughly mixed with hot air led in through the back of the grate *E*, *E*. The large space under the boiler drum gives opportunity for complete combustion of the products under the chimney. The water in the drum circulates through the tubes as shown by the arrows and thus is heated to a high temperature.

Calorific value of fuels. The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. The heat evolved by the combustion of one gram of a fuel is called its *calorific value*. In large contracts the price paid for a fuel is generally based on its calorific value, as well as upon its adaptability to the use to which it is to be put. The following table will give some average values for a few common fuels:

CALORIFIC VALUE OF FUELS

Wood (air-dried)	about 3800–4000 cal.
Lignite (brown), 8% ash, 12% moisture	about 5400 cal.
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash	about 8300 cal.
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash	about 8700 cal.
Anthracite coal (Connellsville), 12% ash	about 7300 cal.
Coke, 10% ash	about 7300 cal.

In determining the calorific value of a fuel an instrument known as a *bomb calorimeter* is used. This is a strong steel flask lined with platinum or porcelain and provided with a tight-fitting screw cap (Fig. 127). In determining the heat of combustion a weighed sample of the substance is placed on the capsule *A*, oxygen is admitted through the tube *B* until the pressure in the bomb is about 20 atmospheres, and the bomb is then closed and placed in an open calorimeter. The charge is ignited by passing an electric current through the fine iron fuse-wire *C* stretched above the charge. The wire is melted, and the red-hot drop of burning metal falls upon the charge, igniting it. The heat given off during combustion is measured by the rise in temperature of the water surrounding the bomb, which is stirred by the stirrer *D*. A preliminary experiment must be made upon a weighed charge of a substance whose heat of combination is known (such as cane sugar), to determine the heat absorbed by the bomb, together with that due to the melting and combustion of the fuse-wire, and also the loss by radiation.

Fig. 128. An arc furnace

The electric furnace. In recent years electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can be easily reached, whereas the hottest oxyhydrogen flame is not much above 2000°. These furnaces are constructed on one of two general principles.

1. ***Arc furnaces.*** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 128. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc. The electrodes and crucible are surrounded by materials which fuse with great difficulty, such as magnesium oxide, the walls of the furnace being so shaped as to reflect the heat downwards upon the contents of the crucible.

2. ***Resistance furnaces.*** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. In its simplest form it may be represented by Fig. 129. The furnace is merely a rectangular box built up of loose bricks. The electrodes (*E*, *E*), each consisting of a bundle of carbon rods, are introduced through the sides of the furnace. The materials to be heated (*C*) are filled into the furnace up to the electrodes, and a layer of broken coke is arranged so as to extend from one electrode to the other. More of the charge is then placed on top of the coke. In passing through the broken coke the electrical current encounters great resistance. This generates much heat, and the charge surrounding the coke is brought to a very high temperature. The advantage of this type of furnace is that the temperature can be regulated to any desired intensity.

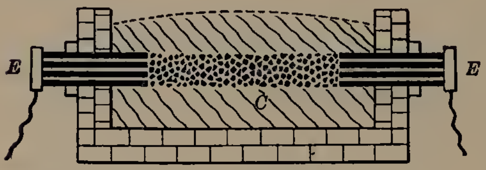


FIG. 129. A resistance furnace

EXERCISES

1. Why does charcoal usually burn with no flame? How do you account for the flame sometimes observed when it burns?

2. How do you account for the fact that a candle burns with a flame?

3. What two properties must the mantle used in the Welsbach lamp possess?

4. (*a*) In what respects does the use of the Welsbach mantle resemble that of lime in the calcium light? (*b*) If the mantle were made of carbon, would it serve the same purpose?

5. Would anthracite coal be suitable for the manufacture of coal gas?

6. How could you prove the formation of carbon dioxide and water in the combustion of illuminating gases?

7. Suggest a probable way in which natural gas has been formed.

8. Coal frequently contains a sulfide of iron. (*a*) What two sulfur compounds are likely to be formed when gas is made from such coal? (*b*) Suggest some suitable method for the removal of these compounds.

9. Why does the use of the bellows on the blacksmith's forge cause a more intense heat?

10. What name is applied to reactions such as those which take place in the manufacture of water gas?

11. Water gas was used as a fuel in a stove which consumed 5 cu. ft. of gas per hour. Calculate the volume of oxygen required to burn the gas, the fuel and oxygen being measured under the same conditions of temperature and pressure.

12. Suppose that natural gas is pure methane and that a stove burns 20 l. of the fuel per hour, measured at 20° and 740 mm. (*a*) What volume of oxygen measured at 20° and 740 mm. would be required for the combustion? (*b*) If a room were heated by the stove and no arrangement was made for carrying off the products of combustion, what volume of carbon dioxide (20° and 740 mm.) would be added to the air in the room? (*c*) What weight of moisture would be formed?

CHAPTER XXVI

CARBOHYDRATES; ALCOHOLS; COAL-TAR COMPOUNDS

Carbohydrates. The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, the last two elements usually being present in the proportion in which they combine to form water. The most important carbohydrates are the following:

TABLE OF CARBOHYDRATES

Sucrose (ordinary sugar)	$C_{12}H_{22}O_{11}$
Lactose (milk sugar)	$C_{12}H_{22}O_{11} \cdot H_2O$
Maltose	$C_{12}H_{22}O_{11} \cdot H_2O$
Dextrose (grape sugar)	$C_6H_{12}O_6$
Levulose	$C_6H_{12}O_6$
Cellulose	$(C_6H_{10}O_5)_x$
Starch	$(C_6H_{10}O_5)_x$

The molecular formulas of cellulose and starch are unknown, but are multiples of the simple formula $C_6H_{10}O_5$; accordingly they are often written $(C_6H_{10}O_5)_x$. In the discussion of the compounds they will be represented by the simple formula $C_6H_{10}O_5$.

It will be noted that some of the compounds named in the table have identical formulas. Such compounds are said to be *isomeric*. The difference in the properties of isomeric compounds is due to the fact that the atoms are arranged differently in the molecule.

Sucrose (sugar) ($C_{12}H_{22}O_{11}$). This substance, commonly called *sugar*, occurs in many plants, especially in the sugar cane and sugar beet, each of which at present furnishes about 50 per cent of the total production. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers), while the sugar beet thrives in cooler climates, such as prevail in Ohio and Michigan in the United States, and in Germany. The beets contain as high as 16 per cent of sucrose.

The manufacture of sugar. The juice from the cane or beet contains the sugar in solution along with many impurities. These impurities are removed by appropriate methods and the resulting solution is then evaporated until the sugar crystallizes. The evaporation is conducted in closed vessels from which the air is partially exhausted (vacuum pans). In this way the boiling point of the solution is lowered and the charring of the sugar is prevented. It is not practicable to remove all the sugar from the solution. Ordinary *molasses* is the solution which remains after a part of the sugar has been crystallized out from the purified juice of the sugar cane. The sweetness of maple sugar is due to sucrose, other products present in the maple sap imparting the distinctive flavor. About 40,000,000,000 lb. of sugar is produced annually. The annual consumption of sugar in the United States is over 9,000,000,000 lb., or approximately 90 lb. for each person.

Chemical conduct of sugar. When a solution of cane sugar is heated to about 70° with hydrochloric acid, two isomeric sugars, *dextrose* and *levulose*, are formed in accordance with the following equation:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

In this process the sugar is said to be *inverted*, and the mixture of dextrose and levulose is termed *invert sugar*.

When heated to 160° sucrose melts; if the temperature is increased to about 215° a partial decomposition takes place and a brown substance known as *caramel* is formed. This is used extensively as a coloring matter and in making confectionery.

Lactose (milk sugar) ($C_{12}H_{22}O_{11} \cdot H_2O$). This compound is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water	87.17%
Casein (nitrogenous matter)	3.56%
Butter fat	3.64%
Lactose	4.88%
Mineral matter	0.75%

When *rennin* (a substance obtained from the stomach of calves) is added to milk the casein separates. This is the part of the milk used in the manufacture of *cheese*. The liquid remaining after the separation of the casein is known as *whey*. This contains the milk sugar, which crystallizes on evaporation; it resembles sucrose in appearance, but is not so sweet nor so soluble. The souring of milk is due to the fact that the milk sugar contained in it changes into *lactic acid*, a liquid having the formula $C_3H_6O_3$:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4\,C_3H_6O_3$$

This change is brought about by a certain microörganism which enters from the air, and the process is known as *lactic fermentation*.

Dextrose (grape sugar, glucose) ($C_6H_{12}O_6$). This sugar is present in honey and in many fruits. It is usually associated with levulose, and is often called *grape sugar* because of its presence in grape juice. It can be obtained along with levulose by heating sucrose with hydrochloric acid, as explained above. Commercially it is prepared in enormous quantities by heating starch with hydrochloric acid. The starch is first changed into a sweet-tasting solid known as *dextrin*, and this, on further action, is converted into dextrose:

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

When the change is complete the hydrochloric acid is neutralized by sodium carbonate. Over 50,000,000 bushels of corn are used each year in the United States in the production of dextrose and allied products.

Pure dextrose is a white crystalline solid resembling sucrose in its properties, but not so sweet. Most of the dextrose used is in the form known commercially as *glucose*, or *corn sirup*. This is a thick sirupy liquid and consists of an aqueous solution of dextrin, dextrose, and maltose. Large quantities of glucose are used in the preparation of jellies, jams, sirups, candy, and other sweets. A federal ruling requires that when glucose is present in such foods as jellies and jams, the label on the container must state the percentage of glucose present.

Starch ($C_6H_{10}O_5$). This substance is always present in seeds and tubers and is by far the most abundant carbohydrate found in nature. In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe the potato serves as the principal source.

The manufacture of starch. In manufacturing starch from corn, the corn is first soaked in water containing a little sulfurous acid, to soften the grain. It is then ground coarsely so as not to crush the germ. When the resulting mass is mixed with water the germ floats, being very light because of the oil which it contains. In this way the germ is separated from the rest of the seed, and from it *corn oil* is prepared. The remaining material, consisting of the starch, the nitrogenous constituent (gluten), and the bran, or outside coating of the grain, is then ground finely, mixed with water, and passed through cloth sieves, which remove the bran. The water containing the starch and gluten in suspension is then allowed to run slowly down long, shallow troughs, the rate of flow being so regulated that the heavier starch sinks to the bottom of the trough while the lighter gluten is washed away. The starch is then removed from the troughs as shown in Fig. 130 and subsequently dried. Large quantities of starch are used in making glucose and other foods, for finishing cloth, and for laundry purposes.

FIG. 130. Removing the starch from the settling troughs in a starch factory

Characteristics of starch. Starch consists of minute granules, which differ somewhat in appearance according to the source of the starch, so that it is often possible from a microscopic examination to determine from what plant any given sample of starch was obtained (Figs. 131 and 132). When heated with water the granules burst and the starch partially dissolves. This is the reason why starchy foods are made more digestible by cooking.

Cellulose ($C_6H_{10}O_5$). Cellulose forms the basis of all woody fibers. Cotton and linen are nearly pure cellulose. It is insoluble in water, alcohol, or dilute acids, but will dissolve in a solution prepared by dissolving copper oxide in ammonium hydroxide. Concentrated hydrochloric acid changes it into dextrose. Concentrated nitric acid forms a mixture of compounds which is known as *nitrocellulose* or *guncotton.* These are very inflammable and under certain conditions are highly explosive. They have many commercial uses. Photographic films are made from them, as well as from a noninflammable derivative of cellulose known as *acetyl cellulose. Collodion* is a solution of certain nitrocelluloses in a mixture of alcohol and ether. *Celluloid* is a mixture of nitrocellulose and camphor. These two when mixed together form a plastic mass which can be molded into any desired shape and which is used for making such objects as combs and brush handles. Celluloid is very inflammable and care should be exercised in the use of celluloid articles.

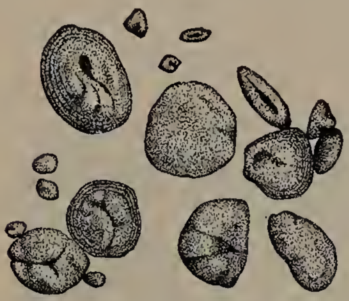


FIG. 131. Wheat-starch granules magnified 200 diameters

Mercerized cotton and artificial silk. When cotton cloth is treated with a concentrated solution of sodium hydroxide, the cellulose shrinks and becomes tougher in character. If the cloth is placed in stretchers to prevent the shrinkage, it assumes an appearance somewhat resembling silk and is known as *mercerized cotton.* Another fabric prepared in large quantities from cellulose resembles silk very closely and is known as *artificial silk.* The fiber of this fabric is prepared by forcing concentrated solutions of cellulose or its derivatives through minute tubes and coagulating the cellulose as it emerges in the form of fine threads.

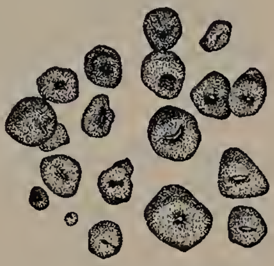


FIG. 132. Cornstarch granules magnified 200 diameters

Characteristics of various textile fibers. Of the different fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are composed of nitrogenous substances. Although these fibers resemble each other when viewed with the naked eye, their appearance is distinctive when examined with the microscope. The characteristic appearance of these fibers is shown in Fig. 133. It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide (5 per cent to 10 per cent) has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk.

Silk fiber Cotton fiber Wool fiber

FIG. 133. Three important textile fibers

Paper. Paper consists mainly of cellulose. The finer grades are made from linen and cotton rags and the cheaper grades from wood.

Manufacture of paper. In making paper the raw material is cut into pieces and treated with suitable reagents (calcium acid sulfite is used in case of wood), to remove all objectionable matter, leaving the cellulose, which is then bleached with chlorine. The paper pulp so obtained is suspended in water and run onto wire screens. It then passes between large iron cylinders, some of which are heated with steam. In this way the pulp is pressed and dried and delivered in the form of paper. In the process different materials are often added to the pulp. These vary with the nature of the paper desired; thus, finely ground clay or calcium sulfate is added to give body to the paper. In making paper intended for writing or printing, a compound prepared by heating resin and sodium hydroxide is added, together with aluminium sulfate. This makes a finished surface and prevents the ink from spreading.

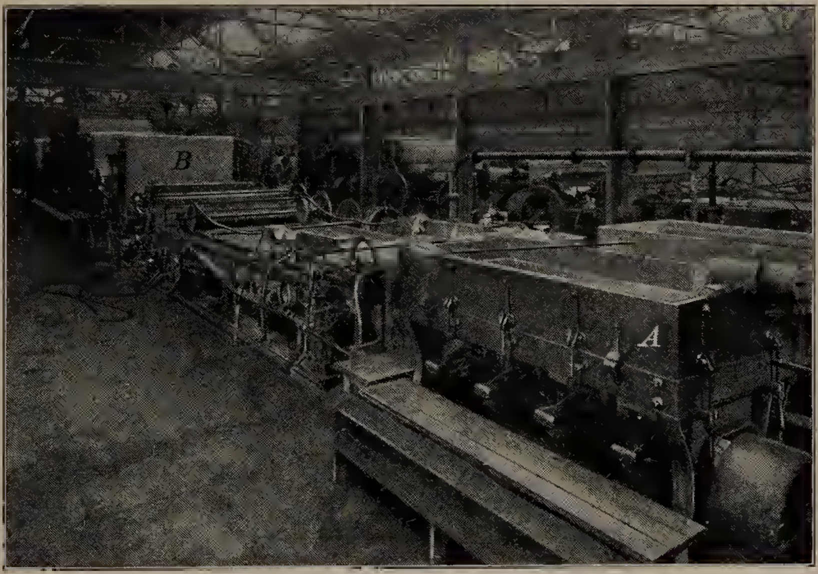


Fig. 134. The interior of a paper mill

Fig. 134 shows the interior of a paper mill. The pulp flows from the container *A* onto the screens beyond and then between the rollers until it is pressed and dried and so converted into the finished paper *B*.

ALCOHOLS

The alcohols may be regarded as derived from the hydrocarbons by substituting for one or more hydrogen atoms a corresponding number of hydroxyl groups. A great many alcohols are known, and, like the hydrocarbons, they may be arranged in series. The relation between the first three members of the methane series of hydrocarbons and the corresponding alcohols is shown in the following table:

CH_4 (methane)	CH_3OH (methyl alcohol)
C_2H_6 (ethane)	C_2H_5OH (ethyl alcohol)
C_3H_8 (propane)	C_3H_7OH (propyl alcohol)

The terms *methyl*, *ethyl*, and *propyl*, used in designating the different alcohols, are names applied to the univalent radicals CH_3, C_2H_5, and C_3H_7 respectively. It will be noted that the names of these radicals are derived from the names of the corresponding hydrocarbons by changing the ending *-ane* to *-yl*.

Methyl alcohol (wood alcohol) (CH_3OH). This compound is formed when wood is heated in the absence of air (p. 121), and on this account it is called *wood alcohol*. It is a colorless liquid which boils at 64.7° and burns with an almost colorless flame. It is a good solvent for organic substances and is used extensively in the manufacture of varnishes. It is poisonous. It also has a specific action on the optic nerve, and many persons have become blind from drinking the liquid or from repeatedly inhaling its vapor.

When a mixture of the vapor of methyl alcohol and air is passed over hot copper, the alcohol is oxidized, forming a gaseous compound known as *formaldehyde*:

$$2\,CH_3OH + O_2 \longrightarrow 2\,CH_2O + 2\,H_2O$$

This gas is now prepared in large quantities and used as a disinfectant. A 40 per cent aqueous solution of it is sold under the name of *formalin*.

Ethyl alcohol (grain alcohol, alcohol) (C_2H_5OH). This compound is the one ordinarily known as alcohol. It resembles methyl alcohol in its general properties.

1. ***Preparation.*** It is prepared by the action of ordinary baker's yeast upon different sugars, such as dextrose:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

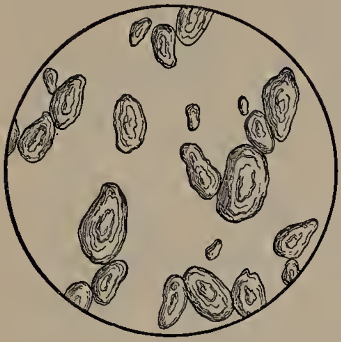


FIG. 135. Some cells of the yeast plant

This process in which a sugar is changed into alcohol and carbon dioxide by the action of yeast is known as *alcoholic fermentation.* The yeast is a low form of plant life (Fig. 135) and thrives in appropriate sugar solutions. During its growth a number of changes take place which result in converting the sugar into alcohol.

Experimental preparation of alcohol. The formation of alcohol and carbon dioxide from dextrose may be shown as follows: A 10 per cent solution of the sugar in water is poured into flask *A* (Fig. 136) and a little baker's yeast is added. The bottle *B*, containing limewater, is connected as shown in the figure. The tube *C* is filled with pieces of sodium hydroxide to prevent carbon dioxide from entering from the air. The temperature is maintained at about 30°. Action soon begins, as is indicated by the bubbles of carbon dioxide, and continues until the sugar is all fermented. That the escaping gas is carbon dioxide is shown by the precipitate formed in *B*. The alcohol formed is separated by distillation.

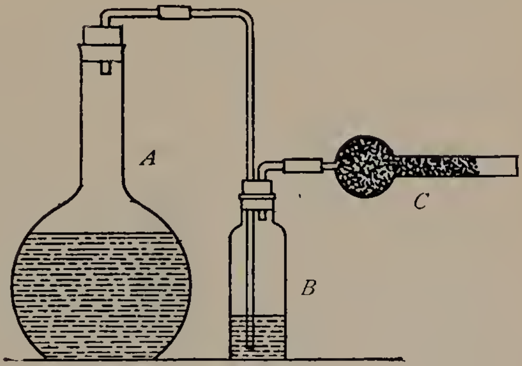


FIG. 136. Laboratory preparation of alcohol

Commercial preparation of alcohol. Alcohol is prepared commercially from starch obtained from corn or potatoes. The starch is first converted into a sugar known as maltose, by the action of *malt*, a substance prepared by moistening barley with water, allowing it to sprout, and then drying it. Maltose, like dextrose, breaks down into alcohol and carbon dioxide in the presence of yeast. The resulting alcohol is separated by fractional distillation.

2. ***Properties.*** Ethyl alcohol is a colorless liquid with a pleasant odor and is an excellent solvent for many organic substances. It boils at 78.3°. It is sometimes used as a fuel, since its flame is very hot and does not deposit carbon, as the flame from oil does. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The ordinary alcohol of the druggist contains about 95 per cent alcohol and 5 per cent water. A solution containing 99 per cent or more of alcohol is called *absolute alcohol*. When alcohol is heated with sulfuric acid a low-boiling inflammable liquid known as *ether* is formed:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

This is largely used as an anesthetic in surgical operations and as a solvent in chemical industries.

Denatured alcohol. While ordinary alcohol (95 per cent) is not difficult to prepare, its selling price is greatly increased because of the high tax imposed by the government. By an act of Congress in 1906 the tax was removed from *denatured alcohol*; that is, alcohol mixed with some substance which renders it unfit for use as a beverage but does not impair its use for manufacturing purposes. The substance most often used for this purpose is *pyridine* — a vile-smelling compound obtained by heating bones.

Alcoholic liquors. All alcoholic liquors are made by alcoholic fermentation. Wine is made by the fermentation of the dextrose in grape juice and contains from 5 to 15 per cent by volume of alcohol. Beer is made from maltose formed by the action of malt upon starch obtained from various grains, chiefly barley. It contains from 3 to 5 per cent by volume of alcohol. Whisky contains about 50 per cent by volume of alcohol and is made from starch by a process very similar to that described under the commercial preparation of alcohol. Almost any saccharine liquid, such as cider and the juices of fruits in general, undergoes alcoholic fermentation when exposed to air.

Alcoholic liquors, as well as pure alcohol, are taxed by the government. Previous to the passage of the prohibition amendment over $200,000,000 was collected annually from this source.

Chemical changes in bread-making. The average composition of wheat flour is as follows:

Water	13.8%
Protein (nitrogenous matter)	7.9%
Fats	1.4%
Starch	76.4%
Mineral matter	0.5%

In making bread, flour is mixed with water, yeast, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. In baking bread the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become porous and making the bread light.

Preservatives. We have observed that the changes taking place in the souring of milk and the changing of sugar into alcohol are caused by organisms the cells of which are present in the air. Many other similar changes, such as putrefaction, are due to the same causes. All these changes may be prevented in one of the following ways:

1. By keeping the substance at such a low temperature that the organism causing the change cannot thrive (cold storage).

2. The substance may be heated so as to destroy all organisms present and then sealed air-tight in a suitable container. This is the method used in canning vegetables and in preserving such substances as grape juice and condensed milk.

3. Some substance may be added which in small amounts will destroy the organisms causing the change or will prevent their growth. Such a substance is known as a *preservative.*

Whether or not preservatives should be permitted in foods is a much-debated question. Some people maintain that any substance which is powerful enough to prevent the growth of the organisms must have an injurious action upon digestion. The federal government at present allows the use of *sodium benzoate* (a white solid made from a hydrocarbon present in coal tar) in such foods as jellies, jams, and catchup, which are not consumed immediately upon the opening of the container. If this preservative is used, however, the labels on the containers must state the amount present.

Some derivatives of coal tar. In discussing the manufacture of coal gas (p. 306) it was stated that from the coal tar formed in the process there is obtained a large number of important compounds. These are often spoken of collectively as the *coal-tar compounds.* It is possible here to mention only a few of these.

(1) *Benzene* (C_6H_6) and (2) *toluene* (C_7H_8) are highly inflammable colorless liquids; (3) *naphthalene* ($C_{10}H_8$) and (4) *anthracene* ($C_{14}H_{10}$) are white, solid hydrocarbons which are used in the preparation of the two dyes indigo and alizarin. These dyes were formerly obtained from vegetable sources, but are now manufactured at low cost. Ordinary moth balls are nearly

pure naphthalene. (5) *Phenol*, or *carbolic acid* (C_6H_5OH), is a white crystalline solid, very caustic and poisonous. (6) *Cresol* (C_7H_7OH) is a good disinfectant and is the basis of most of the disinfectants now on the market.

Each of the above compounds serves as the source material from which many other useful compounds are prepared. Thus, benzene when treated with nitric acid gives *nitrobenzene* ($C_6H_5NO_2$), and this on reduction yields *aniline* ($C_6H_5NH_2$). Aniline is a nearly colorless liquid, and from it are prepared a large number of dyes of all shades and colors, known as the *aniline dyes*. Toluene when oxidized forms *benzoic acid*, the sodium salt of which (*sodium benzoate*) is used as a food preservative. When phenol is heated with formaldehyde there are obtained products known commercially as *bakelite* and *condensite*. These are useful materials for making buttons, umbrella handles, pipestems, and insulators in electrical apparatus.

Coal-tar compounds in foods. Much discussion has arisen in regard to the use of coal-tar compounds in foods. It is evident that no substance which acts injuriously upon the human system should be used in our foods; neither should the law permit the use of any substance which is used for purposes of deception. The federal government has selected seven aniline dyes of different colors, the use of which is permitted in such foods as candies and butter. The use of sodium benzoate as a preservative is allowed under certain restrictions. *Saccharine*, a white solid prepared from toluene and 500 times as sweet as sugar, was formerly permitted in foods, but in 1912 the government forbade its further use. *Vanillin*, identical with the compound prepared from vanilla beans, and *coumarin*, which has an odor similar to vanillin, are both used in artificial vanilla extracts, but when they are so used the label on the container must state the fact. It is well to keep in mind that these substances have no nutritive value.

EXERCISES

1. What is the meaning of the term *carbohydrate*? (See dictionary.)

2. Can you tell the difference between pure sugar obtained from sugar cane and that obtained from the sugar beet?

3. It is often said that milk sours readily during thunder showers. What would you say as to the truth of this statement?

4. Why do we use corn rather than dextrose in making alcohol?

5. How could you tell the difference between methyl alcohol and ethyl alcohol?

6. Yeast is often added in preparing household beverages such as root beer. Why is it added? What substance will be present in the beverage so prepared?

7. Why is sugar (or molasses) added in making bread?

8. Alcohol and gasoline boil at about the same temperature and both are combustible. Why not use alcohol as a fuel in place of gasoline?

9. Can you suggest a method for obtaining ethyl alcohol from wood?

10. What weight of starch is necessary in making 100 kg. of pure dextrose?

11. 1 kg. of sucrose would yield what weight of invert sugar?

12. What weight of dextrose is necessary for the preparation of 10 kg. of the ordinary alcohol of the druggist, on the supposition that 95 per cent of the sugar undergoes fermentation?

13. What weight of benzene is necessary for the preparation of 100 kg. of aniline?

14. What volume of carbon dioxide is evolved in the fermentation of 100 g. of dextrose?

15. What weight of methyl alcohol would be required for the preparation of 50 kg. of formaldehyde?

16. Calculate the weight of lactic acid formed in the souring of 10 kg. of milk.

CHAPTER XXVII

ORGANIC ACIDS; FATS AND OILS

Organic acids. A great number of acids are known which are composed of carbon, oxygen, and hydrogen, and as a group these are called *organic acids.* Like the hydrocarbons, they can be arranged in series, one of the most important of which is known as the *fatty-acid series.* A few of the most important members of this series are given in the following table. They are all monobasic — a fact indicated in the formula by separating the replaceable hydrogen atom from the rest of the molecule.

SOME FATTY ACIDS

$H \cdot CHO_2$	formic acid, a liquid boiling at 100°
$H \cdot C_2H_3O_2$	acetic acid, a liquid boiling at 118°
$H \cdot C_4H_7O_2$	butyric acid, a liquid boiling at 163°
$H \cdot C_{16}H_{31}O_2$	palmitic acid, a solid melting at 62°
$H \cdot C_{18}H_{35}O_2$	stearic acid, a solid melting at 69°
$H \cdot C_nH_{2n-1}O_2$	general formula

Of these acetic acid deserves special mention.

Acetic acid ($H \cdot C_2H_3O_2$). This is the acid which gives the sour taste to vinegar. It is prepared commercially by the distillation of wood (p. 120). It is a colorless liquid and has a strong, pungent odor. When anhydrous it crystallizes as a white solid which melts at 17° and closely resembles ice in appearance; hence the name *glacial* acetic acid. Many of the salts of acetic acid are well-known compounds. Thus, lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$) is the white solid known as *sugar of lead.*

Vinegar. As is well known, when cider is exposed to the air it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider first undergoes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic acid, the necessary oxygen coming from the air. This oxidation is brought about through the action of the microörganism known as *Mycoderma aceti.* This organism is present in the so-called *mother of vinegar.* The oxidation of alcohol into acetic acid through the agency of the *Mycoderma aceti* is known as *acetic fermentation*, and may be represented as follows:

$$C_2H_5OH + O_2 \longrightarrow H \cdot C_2H_3O_2 + H_2O$$

Fig. 137. A generator for the manufacture of vinegar

The manufacture of vinegar. The old method of making vinegar consisted simply in storing cider in barrels until the fermentation was complete. In the modern method a large cask, known as a *generator*, is used (Fig. 137). This is filled loosely with beech shavings. Vinegar is first sprayed into the top of the cask in order to introduce the *Mycoderma aceti.* The organism attaches itself to the wood shavings, which are used because they present a large surface. Next a dilute solution of alcohol (hard cider, in the case of cider vinegar) is sprayed into the top of the cask while air is admitted at the bottom *A*, *A*. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom (*B*) of the cask. Instead of starting with cider, one may use almost any substance which contains starch or sugar, these compounds first being changed into alcohol, as explained in the manufacture of alcohol. In this way are prepared *malt vinegar* from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from pure dilute alcohol, and is known as *distilled vinegar.* It is colorless and leaves no residue upon evaporation.

A federal law requires that all vinegar shall contain not less than 4 per cent acetic acid. In addition to the acid, vinegar prepared from fruits and grains contains certain solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

Acids belonging to other series. In addition to the fatty acids, the following deserve special mention:

Tartaric acid ($H_2 \cdot C_4H_4O_6$). This is a white solid and occurs in many fruits, either in the free state or in the form of its salts. The acid potassium salt $KHC_4H_4O_6$ occurs in the juice of grapes. When the juice ferments in the manufacture of wine, this salt, being insoluble in alcohol, is deposited on the sides of the cask, in which form it is known as *argol.* When purified it forms a white solid, which is sold under the name of *cream of tartar* and is used in baking powders. The acid itself is often used in soft drinks.

Citric acid ($H_3 \cdot C_6H_5O_7$). This acid occurs in citrus fruits, such as lemons and grape fruit. It is a white solid, soluble in water.

Oleic acid ($H \cdot C_{18}H_{33}O_2$). The derivatives of this acid constitute the principal part of many oils and liquid fats. The acid itself is an oily liquid.

Fats and oils. The hydrogen of acids can be replaced not only by metals but by *hydrocarbon radicals* as well. The resulting compounds are termed *esters.* The main constituents of the common fats and oils, such as butter, lard, and olive oil, are esters of *oleic*, *palmitic*, and *stearic* acids and are known respectively as *olein*, *palmitin*, and *stearin*. The radical present in these esters is C_3H_5. It is trivalent and is known as the *glyceryl* radical, since it is present in *glycerin* ($C_3H_5(OH)_3$). Since the glyceryl radical is trivalent, and since oleic, palmitic, and stearic acids are all monobasic, it is evident that three molecules of each acid must enter into the formation of each molecule of the ester derived from it. The relation in composition between these acids and the corresponding esters is shown in the following formulas:

$H \cdot C_{18}H_{33}O_2$ (oleic acid)	$C_3H_5(C_{18}H_{33}O_2)_3$ (olein)
$H \cdot C_{16}H_{31}O_2$ (palmitic acid) . . .	$C_3H_5(C_{16}H_{31}O_2)_3$ (palmitin)
$H \cdot C_{18}H_{35}O_2$ (stearic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (stearin)

Olein is a liquid and is the main constituent of oils such as olive oil. Palmitin and stearin are white solids. Beef suet is principally stearin.

Butter fat and oleomargarine. While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of a small amount (about 8 per cent) of the fat *butyrin*, which is an ester of butyric acid and has the formula $C_3H_5(C_4H_7O_2)_3$. Oleomargarine differs from butter mainly in the fact that a smaller amount of butyrin is present. It is made from the fats obtained from cattle and hogs. Sometimes cottonseed oil is also added. These fats are churned with milk or mixed with a small amount of butter, in order to furnish sufficient butyrin to give the butter flavor.

In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the federal tax has been paid.

Changing oils into solid fats. It will be noted that stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule. Now if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalytic agent (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. It is possible in this way to change the oils into solid fats. Certain commercial fats used in cooking are made by this process from the comparatively inexpensive cottonseed oil.

The proteins. The term *protein* is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms and which constitute the principal part of the tissues of the living cell. The casein of milk, gluten of flour, and albumin of egg will serve as examples of protein matter. The proteins all contain nitrogen, carbon, hydrogen, and oxygen, and some contain sulfur and phosphorus in addition.

Foods. While the compounds present in our foods are very numerous and often exceedingly complex, yet they may all be included in a few general classes. It is customary to regard the edible portion of our foods as composed of proteins, fats, carbohydrates, mineral matter, and water. Since the mineral matter is left as a residue when the food is burned, it is listed as ash in reporting the analyses of foods.

In a general way it may be stated that the proteid matter in our food serves to replace the worn-out tissues of our bodies, as well as to supply material for growth. The carbohydrates and fats are more or less interchangeable, since both are oxidized in the body and serve as a source of heat and muscular energy. The mineral matter supplies the material for building up the solid tissues of the body and has, in addition, other more complex functions. The proteid matter may fulfill the same function as the fats and carbohydrates if the latter are lacking in our foods. Since the various constituents of our foods serve different purposes, it is evident that a proper mixture of these is essential to health.

The composition of the edible portion of a few typical foods is given in the following table, taken from Sherman's "Chemistry of Food and Nutrition."

	WATER (Per cent)	PROTEIN (Per cent)	FAT (Per cent)	CARBOHYDRATES (Per cent)	ASH (Per cent)
Beef free from visible fat	73.8	22.1	2.9		1.2
Ham, smoked, lean . .	53.5	20.2	20.8		5.5
Salmon	64.6	21.2	12.8		1.4
Eggs	73.7	14.8	10.5		1.0
Milk	87.0	3.3	4.0	5.0	0.7
Butter	11.0	1.0	85.0		3.0
Oatmeal	7.3	16.1	7.2	67.5	1.9
Rice	12.3	8.0	0.3	79.0	0.4
Wheat flour	11.9	13.3	1.5	72.7	0.6
Bread, white	35.3	9.2	1.3	53.1	1.1
Beans, dried	12.6	22.5	1.8	59.6	3.5
Corn, green	75.4	3.1	1.1	19.7	0.7
Potatoes	78.3	2.2	0.1	18.4	1.0
Tomatoes	94.3	0.9	0.4	3.9	0.5
Apples	84.6	0.4	0.5	14.2	0.3

The cycle of carbon in nature. By means of the energy supplied by sunlight the carbon dioxide absorbed from the air by plants reacts with water and small amounts of other substances derived from the soil to form complex compounds of carbon which constitute the essential part of the plant tissue. This reaction is attended by the evolution of oxygen, which is restored to the air. The compounds resulting from these changes are much richer in energy than are the substances from which they are formed, the source of this energy being the sunshine.

If the plant is burned or decays in the open air, the changes which took place in the formation of the constituents of the plant are largely reversed. The carbon and hydrogen combine with oxygen taken from the air to form carbon dioxide and water, while the energy absorbed from the sun's rays is liberated in the form of heat. If, on the other hand, the plant is used as food, the compounds present are utilized in building up the tissues of the body and as a source of energy. In either case the carbon and hydrogen ultimately combine with inhaled oxygen to form carbon dioxide and water, which are in turn exhaled. The energy possessed by the food substance is liberated partly in the form of heat, which maintains the temperature of the body, and partly as muscular energy. The carbon dioxide originally absorbed from the air by the plant is thus restored, and the cycle of changes begins anew.

EXERCISES

1. For what purpose have we used formic acid? Consult the dictionary for the derivation and significance of the word *formic.*

2. What weight of dextrose would be required to prepare 100 kg. of vinegar containing the legal quantity of acetic acid, on the supposition that all the sugar is converted into acetic acid?

3. Account for the fact that potassium-acid tartrate separates when grape juice ferments.

4. Aluminium is a trivalent metal. Write the formula for aluminium stearate; aluminium tartrate; aluminium citrate.

CHAPTER XXVIII

THE PHOSPHORUS FAMILY

NAME OF ELEMENT	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Phosphorus	P	31.04	1.8	44°
Arsenic	As	74.96	5.73	850°
Antimony	Sb	120.2	6.52	630°
Bismuth	Bi	208.0	9.8	271°

The family. The elements constituting this family belong in the same group with nitrogen and therefore resemble it in a general way in the type of compounds formed. They exhibit the gradation of physical properties shown in the above table. The same general gradation is also found in their chemical characteristics, phosphorus being an acid-forming element, while bismuth is essentially a metal. The other two elements are intermediate in character.

Compounds. In general the elements of the family form compounds having similar composition, as is shown in the following table:

PH_3	PCl_3	PCl_5	P_2O_3	P_2O_5
AsH_3	$AsCl_3$	$AsCl_5$	As_2O_3	As_2O_5
SbH_3	$SbCl_3$	$SbCl_5$	Sb_2O_3	Sb_2O_5
	$BiCl_3$	$BiCl_5$	Bi_2O_3	Bi_2O_5

In the case of phosphorus, arsenic, and antimony the oxides are acid anhydrides. Salts of at least four acids of each of these three elements are known, the free acid in some instances being unstable. The relation of these acids to the corresponding anhydrides may be illustrated as follows, phosphorus being taken as an example:

$P_2O_3 + 3\,H_2O \longrightarrow 2\,H_3PO_3$ (phosphorous acid)
$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$ (phosphoric acid)
$P_2O_5 + 2\,H_2O \longrightarrow H_4P_2O_7$ (pyrophosphoric acid)
$P_2O_5 + H_2O \longrightarrow 2\,HPO_3$ (metaphosphoric acid)

Phosphorus

History. The element phosphorus was discovered by the alchemist Brand, of Hamburg, in 1669, while searching for the philosophers' stone. Owing to its peculiar properties and the secrecy which was maintained about its preparation, it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale.

Occurrence. Owing to its great chemical activity phosphorus never occurs free in nature. In the form of phosphates it is very abundant and widely distributed. *Phosphorite* is the chief mineral form of calcium phosphate, while *apatite* consists of calcium phosphate together with calcium fluoride or calcium chloride. These minerals form very large deposits and are extensively mined for use as fertilizers. Calcium phosphate is a constituent of all fertile soil, having been supplied to the soil by the disintegration of rocks containing it. It is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

Preparation. Phosphorus is now manufactured from bone ash or a pure mineral phosphate by heating the phosphate with sand and carbon in an electric furnace. Sand consists largely of silica (SiO_2), and this is the anhydride of metasilicic acid (H_2SiO_3). At very high temperatures phosphoric anhydride (P_2O_5) is volatile, while at the same temperature silica is not. Consequently when calcium phosphate is heated with silica the following equilibrium is set up:

$$Ca_3(PO_4)_2 + 3\,SiO_2 \rightleftarrows 3\,CaSiO_3 + P_2O_5$$

The phosphoric anhydride formed in the reaction is then reduced by the carbon, as follows:

$$2\,P_2O_5 + 10\,C \longrightarrow P_4 + 10\,CO$$

The materials are fed in at *A* (Fig. 138) by the feed screw *B*. The phosphorus vapor escapes at *D* and is condensed under water, while the calcium silicate is tapped off as a liquid at *C*. The phosphorus obtained in this way is quite impure and is purified by distillation or by melting it and pressing it through cloth.

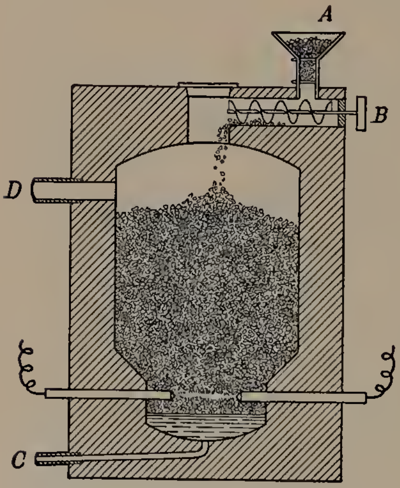


FIG. 138. A furnace for the production of phosphorus

Properties. The purified phosphorus, called *white*, or *yellow, phosphorus*, is a nearly colorless, translucent, waxy solid which melts at 44° and boils at 287°. It can therefore be cast into any convenient form under warm water, and is usually sold on the market in the form of sticks (Fig. 139). It can be cut with a knife, but this must always be done under water, since phosphorus is extremely inflammable, and the friction of the knife blade is almost sure to set it on fire if it is cut in the air. It is not soluble in water, but is freely soluble in some other liquids, notably in carbon disulfide.

Its density is 1.8. One gram-molecular volume (22.4 l.) of phosphorus vapor weighs about 128 g., which is approximately four times the atomic weight, showing that the formula of the molecule is P_4.

Chemical conduct. When exposed to the air, phosphorus slowly combines with oxygen and in so doing gives out a pale light, or *phosphorescence*, which can be seen only in a dark place. The heat of the room may raise the temperature of phosphorus to the kindling point, when it burns with a sputtering flame, giving off dense fumes of oxide of phosphorus. It burns with dazzling brilliancy in oxygen and combines directly with many other elements. On account of its great attraction for oxygen it is preserved under water.

Phosphorus is very poisonous, from 0.2 to 0.3 g. being a fatal dose. Ground with flour and grease or similar substances, it is used as a poison for rats and other vermin.

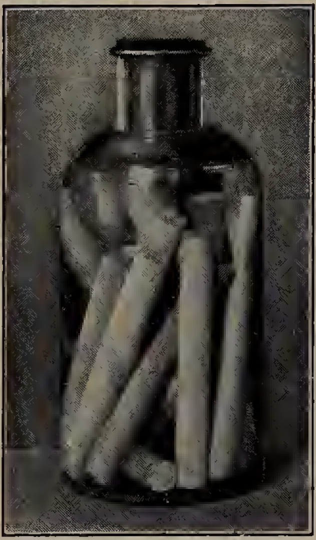


FIG. 139. Sticks of white phosphorus

Red phosphorus. On standing, white phosphorus gradually undergoes a remarkable change, being converted into a dark-red powder which has a density varying from 2.1 to 2.38 and which is called *red phosphorus.* It no longer takes fire easily, nor is it soluble in carbon disulfide. It is not poisonous and, in fact, is an entirely different substance. The velocity of this change of white phosphorus to red phosphorus increases with rise in temperature, and red phosphorus is therefore prepared by heating the white form a little below the boiling point. When distilled and quickly condensed, the red form changes back to the white. This is in accordance with the general rule that when a substance capable of existing in several forms is condensed from a gas or crystallized from the liquid state, the more unstable variety forms first, and this then passes into the more stable forms.

Matches. The chief use of phosphorus is in the manufacture of matches, two general varieties of which are in common use. Ordinary friction matches are made by dipping the match sticks first into some inflammable substance, such as melted paraffin, and afterward into a paste consisting of (1) phosphorus sesquisulfide (P_4S_3), (2) some oxidizing substance, such as manganese dioxide or potassium chlorate, and (3) a binding material, usually some kind of glue. The phosphorus sulfide is ignited by friction, the combustion being sustained by the oxidizing agent and communicated to the wood by the burning paraffin. In sulfur matches the paraffin is replaced by sulfur.

In safety matches a mixture of *red* phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, is placed on the side of the box, while the match tip is provided with an oxidizing agent and an easily oxidizable substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface.

Matches were formerly made from white phosphorus, and the workmen frequently suffered from dreadful diseases of the bones of the face. On this account the manufacture and use of matches containing white phosphorus was prohibited in European countries. The compound P_4S_3, which is easily prepared from white phosphorus, serves just as well and does not occasion disease, and in 1913 the government of the United States placed a prohibitive tax (two cents per hundred matches) on the white phosphorus match, at the same time forbidding both the import and the export of such matches.

Hydrides of phosphorus — phosphine. Phosphorus forms several compounds with hydrogen, the best known of which is *phosphine* (PH_3) analogous to ammonia (NH_3).

The simplest way of making phosphine is to treat calcium phosphide with water:

$$Ca_3P_2 + 6\,H_2O \longrightarrow 3\,Ca(OH)_2 + 2\,PH_3$$

It is more conveniently made by boiling white phosphorus suspended in a concentrated solution of sodium hydroxide, the reaction being a complicated one:

$$P_4 + 3\,NaOH + 3\,H_2O \longrightarrow 3\,NaH_2PO_2 + PH_3$$

Phosphine is a gas of unpleasant odor and is exceedingly poisonous. Like ammonia, it forms salts with the halogen acids. Thus, we have phosphonium chloride (PH_4Cl) analogous to ammonium chloride (NH_4Cl). The phosphonium salts are of but little importance.

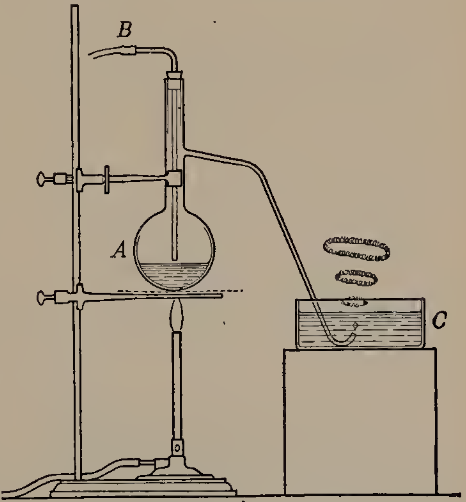


Fig. 140. The preparation of phosphine

Phosphine can be conveniently made in the apparatus shown in Fig. 140. A concentrated solution of sodium hydroxide together with several small bits of phosphorus are placed in the flask *A*, and a current of coal gas is passed into the flask through the tube *B* until all the air has been displaced. The gas is then turned off and the flask is heated. Phosphine is formed in small quantities and escapes through the delivery tube, the exit of which is just covered by the water in the vessel *C*. Each bubble of the gas as it escapes into the air takes fire, and the product of the combustion (P_2O_5) forms beautiful rings, which float unbroken for a considerable time in quiet air. The pure phosphine does not take fire spontaneously. When prepared as directed above, a second hydride of phosphorus (P_2H_4) is present which imparts this property.

Oxides of phosphorus. Phosphorus forms two well-known oxides — the trioxide (P_2O_3) and the pentoxide (P_2O_5), sometimes called phosphoric anhydride. When phosphorus burns in an insufficient supply of air the product is partially the trioxide; in oxygen or an excess of air the pentoxide is formed. The pentoxide is much the better known of the two. It is a snow-white voluminous powder whose most marked property is its great attraction for water. It has no chemical action upon most gases, so that they can be very thoroughly dried by allowing them to pass through properly arranged vessels containing phosphorus pentoxide.

Acids of phosphorus. The important acids of phosphorus are the following:

H_3PO_3	phosphorous acid
H_3PO_4	phosphoric acid
$H_4P_2O_7$	pyrophosphoric acid
HPO_3	metaphosphoric acid

These may be regarded as combinations of the oxides of phosphorus with water according to the equations given in the discussion of the characteristics of the family (p. 347).

1. ***Phosphorous acid*** (*H_3PO_3*). Neither the acid nor its salts are at all frequently met with in chemical operations. It can be easily obtained, however, in the form of transparent crystals when phosphorus trichloride is treated with water and the resulting solution evaporated:

$$PCl_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HCl$$

It is a powerful reducing agent because of its tendency to take up oxygen and pass over into phosphoric acid.

2. ***Orthophosphoric acid (phosphoric acid) (H_3PO_4).*** This acid can be obtained by dissolving phosphorus pentoxide in boiling water, as represented in the equation

$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$$

It is usually made by treating calcium phosphate with concentrated sulfuric acid. The calcium sulfate produced in the reaction is nearly insoluble and can be filtered off, leaving the phosphoric acid in solution. Very pure acid is made by oxidizing phosphorus with nitric acid. It forms large colorless crystals which are exceedingly soluble in water.

Orthophosphates. Since phosphoric acid is a tribasic acid, it forms acid as well as normal salts. Thus the following compounds of sodium are known:

NaH_2PO_4	sodium dihydrogen phosphate
Na_2HPO_4	disodium hydrogen phosphate
Na_3PO_4	normal sodium phosphate

These salts may be prepared by bringing together phosphoric acid and appropriate quantities of sodium hydroxide. Phosphoric acid also forms *mixed* salts, that is, salts containing two different metals. The most familiar compound of this kind is microcosmic salt, which has the formula $Na(NH_4)HPO_4$.

The orthophosphates form an important class of salts. The normal salts are nearly all insoluble and many of them occur in nature. The monohydrogen phosphates are as a rule insoluble, while most of the dihydrogen salts are soluble.

The rock phosphates of Florida and Tennessee contain about seventy per cent of calcium phosphate $Ca_3(PO_4)_2$.

They are mined in large quantities and used in the manufacture of fertilizers (Fig. 141).

3. ***Pyrophosphoric acid*** **($H_4P_2O_7$).** On heating orthophosphoric acid to about 225°, pyrophosphoric acid is formed in accordance with the following equation:

$$2\,H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

It is a white crystalline solid. Its salts can be prepared by heating a monohydrogen phosphate:

$$2\,Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O$$

Fig. 141. Mining phosphate rock in Florida

4. ***Metaphosphoric acid (glacial phosphoric acid)*** **(HPO_3).** This acid is formed when orthophosphoric acid is heated above 400°:

$$H_3PO_4 \longrightarrow HPO_3 + H_2O$$

It is also formed when phosphorus pentoxide is treated with cold water:

$$P_2O_5 + H_2O \longrightarrow 2\,HPO_3$$

It is a white crystalline solid, and is so stable towards heat that it can be fused and even volatilized without decomposition. On cooling from the fused state it forms a glassy solid, and on this account is often called glacial phosphoric acid. It possesses the property of dissolving small quantities of metallic oxides, with the formation of compounds which, in the case of certain metals, have characteristic colors. It is therefore used in the detection of these metals.

While the monohydrogen phosphates, on heating, give salts of pyrophosphoric acid, the dihydrogen phosphates yield salts of metaphosphoric acid. The equations representing these reactions are as follows:

$$2\,Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O,$$
$$NaH_2PO_4 \longrightarrow NaPO_3 + H_2O$$

Sulfides of phosphorus. A number of compounds consisting of phosphorus and sulfur can be obtained by heating the two elements in various proportions. The most important of these has the formula P_4S_3 and is called phosphorus sesquisulfide.

Chlorides of phosphorus. Phosphorus burns readily in chlorine and forms the liquid trichloride, PCl_3, or the solid pentachloride, PCl_5, according to the amount of chlorine available. Both of these compounds have important uses in the preparation of many organic compounds.

ARSENIC

Occurrence. Arsenic occurs in considerable quantities in nature as the native element, as the sulfides realgar (As_2S_2) and orpiment (As_2S_3), as oxide (As_2O_3), and as a constituent of many metallic sulfides, such as arsenopyrite (FeAsS).

Preparation. The element is prepared by purifying the native arsenic or by heating the arsenopyrite in iron tubes, out of contact with air. In the latter case the reaction is expressed by the following equation:

$$4\,FeAsS \longrightarrow 4\,FeS + As_4$$

The arsenic, being volatile, condenses in chambers connected with the heated tubes. It is also made from the oxide by reduction with carbon:

$$2\,As_2O_3 + 3\,C \longrightarrow As_4 + 3\,CO_2$$

Properties and conduct. Arsenic is a steel-gray, metallic-looking substance of density 5.73. Like phosphorus, its molecules contain four atoms (As_4). Though resembling metals in appearance, it is quite brittle, being easily powdered in a mortar. When strongly heated it sublimes; that is, it passes into a vapor without melting, and condenses again to a crystalline solid when the vapor is cooled. Like phosphorus it can be obtained in several allotropic forms. It alloys readily with some of the metals and finds its chief use as an alloy with lead which is used for making shot, the alloy being harder than pure lead and forming rounder drops (shot). When heated on charcoal with the blowpipe, arsenic is converted into an oxide which volatilizes, leaving the charcoal unstained by any oxide coating. It burns readily in chlorine gas, forming arsenic trichloride:

$$As_4 + 6\,Cl_2 \longrightarrow 4\,AsCl_3$$

Unlike most of its compounds, the element itself is not poisonous.

Arsine (AsH_3). When any compound containing arsenic is brought into the presence of nascent hydrogen, arsine (AsH_3), corresponding to phosphine and ammonia, is formed. The reaction when oxide of arsenic is so treated is

$$As_2O_3 + 12\,[H] \longrightarrow 2\,AsH_3 + 3\,H_2O$$

Arsine is a gas with a peculiar garlic-like odor and is intensely poisonous. A single bubble of the pure gas has been known to prove fatal. It is an unstable compound, decomposing into its elements when heated to a moderate temperature. It is combustible and burns with a pale bluish-white flame to form arsenic trioxide and water when air is in excess:

$$2\,AsH_3 + 3\,O_2 \longrightarrow As_2O_3 + 3\,H_2O$$

When the supply of air is deficient, water and metallic arsenic are formed:

$$4\,AsH_3 + 3\,O_2 \longrightarrow 6\,H_2O + As_4$$

These reactions make the detection of even minute quantities of arsenic a very easy problem.

Marsh's test for arsenic. The method devised by Marsh for detecting arsenic is most frequently used. The apparatus is shown in Fig. 142. Hydrogen is generated in the flask *A* by the action of dilute sulfuric acid on zinc, is dried by being passed over calcium chloride in the tube *B*, and after passing through the hard-glass tube *C*, is ignited at the jet *D*. If a substance containing arsenic is now introduced into the generator *A*, the arsenic is converted into arsine by the action of the nascent hydrogen and passes to the jet along with the hydrogen. If the tube *C* is strongly heated at some point near the middle, the arsine is decomposed while passing this point, and the arsenic is deposited just beyond the heated point in the form of a shining brownish-black mirror. A small fraction of a

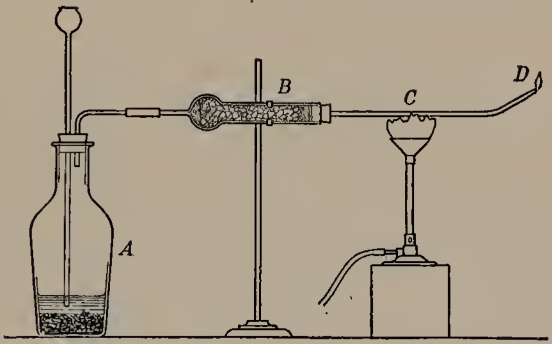


FIG. 142. Marsh's apparatus for the detection of arsenic

milligram of arsenic can be detected by this test. If the tube is not heated, the arsine burns along with the hydrogen at the jet. Under these conditions a small porcelain dish crowded down into the flame is blackened by a spot of metallic arsenic, for the arsine is decomposed by the heat of the flame, and the arsenic, cooled below its kindling temperature by the cold porcelain, deposits upon it as a black spot (p. 317).

Oxides of arsenic. Arsenic forms two oxides, As_2O_3 and As_2O_5, corresponding to the oxides of phosphorus. Of these arsenious oxide, or arsenic trioxide (As_2O_3), is much the better known and is the substance usually called *white arsenic*, or merely arsenic. It is found as a mineral, but is more often obtained as a by-product in various industries in which metallic sulfides are burned in air. The sulfides contain small amounts of arsenic, and when they are burned, arsenious oxide is formed as a vapor together with sulfur dioxide:

$$2\,FeAsS + 5\,O_2 \longrightarrow Fe_2O_3 + As_2O_3 + 2\,SO_2$$

The arsenious oxide is condensed in appropriate chambers. It is obtained either as a white crystalline powder or in large vitreous lumps resembling lumps of porcelain in appearance. It is extremely poisonous, from 0.2 to 0.3 g. being a fatal dose. It is frequently given as a poison, since it is nearly tasteless and does not act rapidly. This slow action is due to the fact that it is not very soluble and hence is absorbed slowly by the system. Arsenious oxide is also used as a chemical reagent in glass making, in the dye industry, and in the manufacture of arsenical insecticides.

Acids of arsenic. Like the corresponding oxides of phosphorus, the oxides of arsenic are acid anhydrides. In solution they combine with bases to form salts corresponding to the salts of the acids of phosphorus. Thus, we have salts of the following acids:

H_3AsO_3	arsenious acid
H_3AsO_4	orthoarsenic acid
$H_4As_2O_7$	pyroarsenic acid
$HAsO_3$	metarsenic acid

Several other acids of arsenic are also known. Not all of these can be obtained as free acids, since they tend to lose water and form the oxides. Thus, instead of obtaining arsenious acid (H_3AsO_3), the oxide As_2O_3 is obtained:

$$2\,H_3AsO_3 \longrightarrow As_2O_3 + 3\,H_2O$$

Salts of all the acids are known, however, and some of them have commercial value. Most of them are insoluble, and some of the copper salts, which are green, are used as pigments. Paris green, which has a complicated formula, is a well-known insecticide. Lead arsenate, whose formula is somewhat variable, is extensively used as a spray on fruit trees.

Sulfides of arsenic. When hydrogen sulfide is passed into an acidified solution containing an arsenic compound the arsenic is precipitated as a bright yellow sulfide, thus:

$$2\,H_3AsO_3 + 3\,H_2S \longrightarrow As_2S_3 + 6\,H_2O$$
$$2\,H_3AsO_4 + 5\,H_2S \longrightarrow As_2S_5 + 8\,H_2O$$

In this respect arsenic resembles the metallic elements, many of which produce sulfides under similar conditions. The sulfides of arsenic, both those produced artificially and those found in nature, are used as yellow pigments.

ANTIMONY

Occurrence. Antimony occurs in nature chiefly as the sulfide (Sb_2S_3), called *stibnite*, though it is also found as the oxide and as a constituent of many complex minerals.

Preparation and properties. Antimony is prepared from the sulfide in a very simple manner. The sulfide is melted with scrap iron in a furnace, when the iron combines with the sulfur to form a liquid layer of melted iron sulfide, while the heavier liquid, antimony, settles to the bottom and is drawn off from time to time. The reaction involved is represented by the equation

$$Sb_2S_3 + 3\,Fe \longrightarrow 2\,Sb + 3\,FeS$$

Antimony is a bluish-white metallic-looking substance whose density is 6.52. It is highly crystalline, hard, and very brittle. It has a rather low melting point (630°) and expands noticeably on solidifying.

Chemical conduct. In chemical properties antimony resembles arsenic in many particulars. It forms the oxides Sb_2O_3 and Sb_2O_5, and in addition Sb_2O_4. It combines with the halogen elements with great energy, burning brilliantly in chlorine to form antimony trichloride ($SbCl_3$). When heated on charcoal with the blowpipe it is oxidized and forms on the charcoal a coating of antimony oxide which has a characteristic bluish-white color.

Stibine (SbH_3). The gas stibine (SbH_3) is formed under conditions which are very similar to those which produce arsine, and it closely resembles the latter compound, though it is still less stable. It is very poisonous.

In Marsh's test for arsenic any antimony that is present is converted into stibine, and this results in a black mirror deposit, as in the case of arsenic. The deposit is more sooty in appearance than is the arsenic deposit, and it is not dissolved by a solution of sodium hypochlorite, whereas the deposited arsenic is dissolved by this reagent.

Acids of antimony. The oxides Sb_2O_3 and Sb_2O_5 are weak acid anhydrides and are capable of forming two series of acids corresponding in formulas to the acids of phosphorus and arsenic. They are much weaker, however, and are of little practical importance.

Sulfides of antimony. Antimony resembles arsenic in that hydrogen sulfide precipitates it as a sulfide when the hydrogen sulfide is conducted into an acid solution containing an antimony compound:

$$2\,SbCl_3 + 3\,H_2S \longrightarrow Sb_2S_3 + 6\,HCl$$
$$2\,SbCl_5 + 5\,H_2S \longrightarrow Sb_2S_5 + 10\,HCl$$

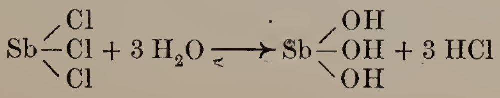
The two sulfides of antimony are called the trisulfide and the pentasulfide respectively. When prepared in this way they are orange-colored substances, though the mineral stibnite is black. The sulfides of antimony are used in the manufacture of matches and of red rubber.

Metallic properties of antimony. The physical properties of the element are those of a metal, and the fact that its sulfide is precipitated by hydrogen sulfide shows that it acts like a metal in a chemical way. Many other reactions show that antimony has more of the properties of a metal than of a nonmetal. The hydroxide, $Sb(OH)_3$, corresponding to arsenious acid, while able to act as a weak acid, is also able to act as a weak base with strong acids. For example, when it is treated with concentrated hydrochloric acid, antimony chloride is formed:

$$Sb(OH)_3 + 3\,HCl \longrightarrow SbCl_3 + 3\,H_2O$$

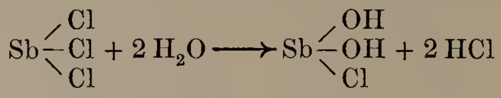
The hydroxides of a number of elements resemble the hydroxide of antimony in that they can act either as a base or as an acid. They are called *amphoteric* hydroxides.

Hydrolysis of antimony salts. Antimony hydroxide, $Sb(OH)_3$, is a very weak base, and we should expect its salts to be decomposed, or hydrolyzed, by water (p. 226). If antimony chloride were to be *completely* hydrolyzed, the equation would be as follows:



$$\mathrm{Sb}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + 3\,H_2O \rightleftarrows \mathrm{Sb}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{matrix} + 3\,HCl$$

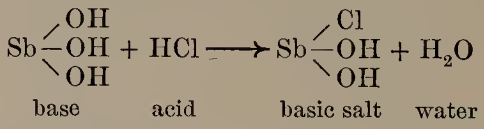
The reaction is not so complete, however, only two of the three chlorine ions being replaced by hydroxyl ions:



$$\mathrm{Sb}\begin{array}{l}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{Sb}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{Cl}\end{array} + 2\,\mathrm{HCl}$$

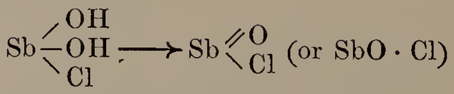
If we wish to prevent this hydrolysis, we must add hydrochloric acid in sufficient quantity to reverse the reaction of hydrolysis by mass action (p. 220).

Basic salts and oxysalts. The compound formed by the partial hydrolysis of antimony chloride is unlike any we have yet met. Since it contains hydroxyl radicals combined with a metal, we must regard it as a *base*; but it also contains a chlorine atom combined with a metal, so that it is likewise a *salt*. Since it has the characteristics of both a base and a salt, it is a *basic salt* (p. 187).



$$\underset{\text{base}}{\mathrm{Sb}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array}} + \underset{\text{acid}}{\mathrm{HCl}} \longrightarrow \underset{\text{basic salt}}{\mathrm{Sb}\begin{array}{l}\diagup\mathrm{Cl}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array}} + \underset{\text{water}}{\mathrm{H_2O}}$$

The basic chloride of antimony easily loses water, as shown in the equation



$$\mathrm{Sb}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{Cl}\end{array} \longrightarrow \mathrm{Sb}\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{Cl}\end{array} \text{ (or } \mathrm{SbO \cdot Cl}\text{)}$$

The resulting compound is at once both an oxide and a salt. It is called antimony oxychloride.

BISMUTH

Occurrence. Bismuth is usually found in the uncombined form in nature. It also occurs as oxide and sulfide. Most of the bismuth of commerce comes from Saxony, from Mexico, and from Colorado, but it is not an abundant element.

Preparation and properties. Bismuth is prepared by merely heating the ore containing the native bismuth and allowing the melted metal to run out into suitable vessels. Other ores are converted into oxides and reduced by heating with carbon.

Bismuth is a heavy, crystalline, brittle metal nearly the color of silver, but with a slightly rosy tint which distinguishes it from other metals. It melts at a low temperature (271°) and has a density of 9.8. It is not acted upon by the air at ordinary temperatures.

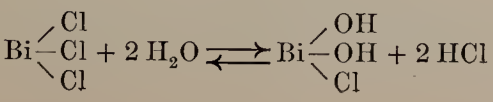
Chemical conduct. When heated with the blowpipe on charcoal, bismuth gives a coating of the oxide Bi_2O_3. This has a yellowish-brown color which easily distinguishes it from the oxides formed by other metals. It combines very readily with the halogen elements, powdered bismuth burning readily in chlorine. It is below hydrogen in the electrochemical series (p. 191), and in the absence of air it is not acted upon by hydrochloric acid.

Compounds of bismuth. Unlike the other elements of this group, bismuth has almost no acid properties. Its chief oxide, Bi_2O_3, is basic in its properties. It dissolves in strong acids and forms salts of bismuth:

$$Bi_2O_3 + 6\,HCl \longrightarrow 2\,BiCl_3 + 3\,H_2O$$
$$Bi_2O_3 + 6\,HNO_3 \longrightarrow 2\,Bi(NO_3)_3 + 3\,H_2O$$

The nitrate and the chloride of bismuth can be obtained as well-formed colorless crystals.

Bismuth hydroxide is a weak base, and its salts, like those derived from antimony hydroxide, undergo partial hydrolysis in dilute solution. Thus, bismuth chloride is hydrolyzed according to the equation



$$\mathrm{Bi}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + 2\,H_2O \rightleftarrows \mathrm{Bi}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{Cl}\end{matrix} + 2\,HCl$$

This action is reversible, and by adding an excess of hydrochloric acid the basic chloride is changed into the normal chloride.

By loss of water the basic chloride is converted into bismuth oxychloride:

$$Bi(OH)_2Cl \longrightarrow BiO \cdot Cl + H_2O$$

In a similar way bismuth nitrate forms the compound $BiO \cdot NO_3$, known as bismuth oxynitrate, or subnitrate.

ALLOYS

Some metals when melted together thoroughly intermix, and on cooling form a metallic-appearing substance called an *alloy.* Not all metals will mix in this way, and in some cases definite chemical compounds are formed and separate out as the mixture solidifies, thus destroying the uniform quality of the alloy. In general, the melting point of the alloy is below the average of the melting points of its constituents, and it is usually lower than that of any one of them.

Alloys of antimony and bismuth. Both antimony and bismuth readily alloy with many other metals. The alloys so formed are heavy, are easily melted, do not oxidize easily nor act upon water, and, in general, are well adapted to many technical uses. The manufacture of alloys constitutes the chief use of these two metals.

Antimony imparts to its alloys the property of expanding slightly in solidification, which renders them especially useful in type founding, where fine lines are to be reproduced on a cast. *Type metal* consists of antimony, lead, and tin. *Babbitt* metal, used for journal bearings in machinery, contains the same metals in a different proportion, together with a small percentage of copper.

Bismuth is particularly valuable in the production of very low-melting alloys. For example, *Wood's metal*, consisting of bismuth, lead, tin, and cadmium, melts at 60.5°. The low melting point of such alloys is turned to practical account in making automatic fire curtains and automatic water sprinklers in buildings, safety plugs in boilers, and many similar devices.

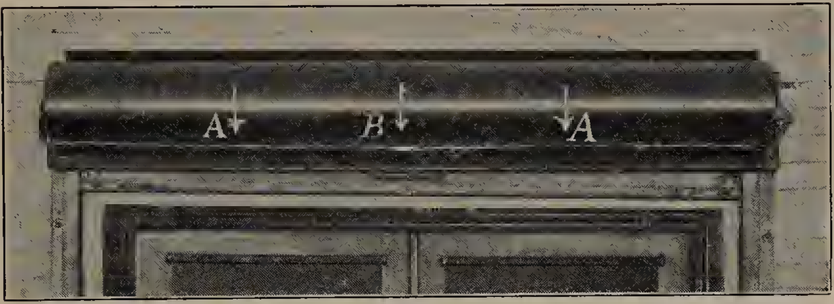


FIG. 143. An automatic fire curtain above a door

Fig. 143 shows a fire curtain, which is held in place by two wires (A, A) joined at B by a bismuth alloy. In case of fire the alloy melts, and the wires holding the curtain up are thereby released and the curtain drops, covering the door.

EXERCISES

1. What is the derivation of the word *phosphorus*?

2. What compounds would you expect phosphorus to form with bromine and iodine? Write the equations showing the action of water on these compounds.

3. In the preparation of phosphine why is coal gas passed into the flask? What other gases would serve the same purpose?

4. Give the formula for the salt which phosphine forms with hydriodic acid. Give the name of the compound.

5. Could phosphoric acid be substituted for sulfuric acid in the preparation of the common acids?

6. Write the equations for the preparation of the three sodium salts of orthophosphoric acid.

7. Why does a solution of normal sodium phosphate show an alkaline reaction?

8. On the supposition that bone ash is pure calcium phosphate, what weight of it would be required in the preparation of 1 kg. of phosphorus?

9. If arsenopyrite is heated in a current of air, what products are formed?

10. (*a*) Write equations for the complete combustion of hydrogen sulfide, methane, and arsine. (*b*) In what respects are the reactions similar?

11. Write the equations for all the reactions involved in Marsh's test for arsenic.

12. Write the names and formulas for the acids of antimony.

13. Write the equations showing the hydrolysis of antimony trichloride; of bismuth nitrate.

14. In what respects does nitrogen resemble the members of the phosphorus family?

15. What weight of arsenic trioxide can be prepared from 1 kg. of arsenopyrite?

16. Suppose you wish to prepare 1 kg. of bismuth oxychloride; what weight of bismuth would be required?

17. What weight of stibnite is necessary for the preparation of 10 kg. of antimony?

CHAPTER XXIX

SILICON; TITANIUM; BORON

NAME OF ELEMENT	SYMBOL	ATOMIC WEIGHT	DENSITY	CHLORIDES	OXIDES
Silicon	Si	28.3	2.35	$SiCl_4$	SiO_2
Titanium	Ti	48.1	4.5	$TiCl_4$	TiO_2
Boron	B	11.0	2.45	BCl_3	B_2O_3

General. Each of the three elements silicon, titanium, and boron belongs to a separate periodic family, but they occur near together in the periodic grouping and are very similar both in properties and in chemical activity. Since the other elements in their families either are so rare that they need not be studied in detail or are best understood in connection with other elements, it is convenient to consider these three together at this point.

SILICON

Occurrence. Next to oxygen, silicon is the most abundant element, for the solid crust of the earth is estimated to contain 28 per cent of this element. All varieties of granite, gneiss, sandstone, shale, clay, and marl contain large percentages of silicon — limestone and dolomite being the only important geological formations measurably free from it. To some extent its compounds are assimilated by plants and animals, and silicon compounds constitute the outer shell of many aquatic organisms.

The element. In the laboratory crystallized silicon is best prepared by the reduction of the dioxide with aluminium:

$$3\,SiO_2 + 4\,Al \longrightarrow 3\,Si + 2\,Al_2O_3$$

The silicon dissolves in the excess of melted aluminium, and when the solution has cooled and become solid, the aluminium is dissolved in hydrochloric acid, the silicon being left in the form of shining metallic needles. The reduction of the dioxide with carbon has always presented the difficulty that the reduced element tends to combine with excess of carbon to form a carbide. This difficulty has been overcome to a great extent, and nearly pure silicon is now manufactured in large quantities. By reducing a mixture of the oxides of silicon and iron with carbon, an alloy of the two elements, called *ferrosilicon*, is obtained. This alloy, as well as the purer silicon, finds an important application in the metallurgy of iron.

Properties. The element presents a close analogy with carbon in that it can be obtained in amorphous form, as well as in crystals resembling the diamond. These crystals are very hard, easily scratching glass, and have a density of 2.35. They melt at about 1420°. A lump of the element is very brittle and breaks with a crystalline fracture which has a metallic, silvery appearance.

At ordinary temperatures silicon is inactive. At high temperatures it combines with most elements, forming *silicides*, such as those of magnesium (Mg_2Si) and carbon (CSi).

Compounds of silicon with hydrogen and the halogens. Silicon hydride (SiH_4) corresponds in formula to methane (CH_4), but its properties are more like those of phosphine (PH_3). It is a very inflammable gas of disagreeable odor and, as ordinarily prepared, takes fire spontaneously on account of the presence of impurities.

Silicon combines with the elements of the chlorine family to form such compounds as $SiCl_4$ and SiF_4. Of these silicon fluoride (SiF_4) is the most familiar and interesting. As stated in the discussion of fluorine, it is formed when hydrofluoric acid acts on silicon dioxide or on a silicate. With silica the reaction is thus expressed:

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4 + 2\,H_2O$$

Silicon fluoride is a very volatile, invisible, poisonous gas. In contact with water it is partially decomposed, as shown in the equation

$$SiF_4 + 4\,H_2O \longrightarrow 2\,H_2F_2 + Si(OH)_4$$

The hydrofluoric acid so formed combines with an additional amount of silicon fluoride, forming the complex fluosilicic acid (H_2SiF_6), thus:

$$H_2F_2 + SiF_4 \longrightarrow H_2SiF_6$$

Silicides. As the name indicates, silicides are compounds consisting of silicon and some one other element. They are very stable at high temperatures and are usually made by heating the appropriate substances in an electric furnace.

The most important silicide is *carborundum*, which is a silicide of carbon of the formula CSi. It is made by heating coke and sand in an electric furnace, the process being extensively carried on at Niagara Falls. The following equation represents the reaction:

$$SiO_2 + 3\,C \longrightarrow CSi + 2\,CO$$

The substance so prepared consists of beautiful purplish-black crystals, which are surpassed in hardness only by a few substances, such as the diamond and boron carbide. Carborundum is used as an abrasive; that is, as a material for grinding and polishing very hard substances.

Fig. 144 shows two samples of the crystalline material, as well as a whetstone and a grinding wheel prepared from carborundum, illustrating some of its many uses.

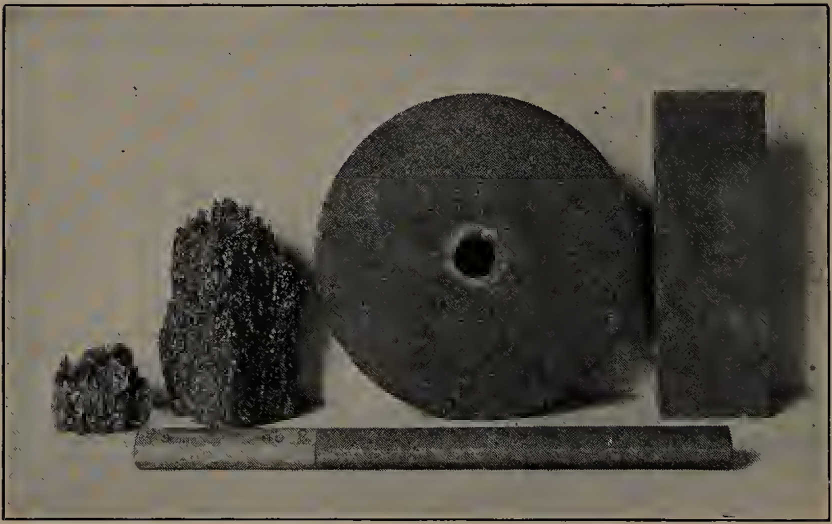


Fig. 144. Crystals of carborundum and abrasive utensils made of carborundum

Manufacture of carborundum. The mixture of materials is heated in a large resistance furnace, similar to the one employed in the manufacture of graphite (p. 119). Fig. 145 represents a cross section of the furnace after charging, A being the carbon core and B the coke and sand. Fig. 146 shows the appearance after heating. A is the core of carbon, surrounded by crystallized carborundum B. Around this is a shell of amorphous carborundum C, while D is unchanged charge.

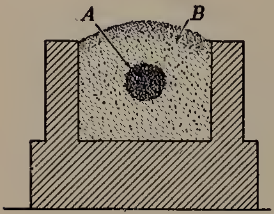


Fig. 145. Cross section of a charged carborundum furnace before being heated

Silicon dioxide (silica) (SiO_2). This substance is found in a great variety of forms in nature, both in the amorphous and in the crystalline condition. In the form of *quartz* (Fig. 147) it is found in beautifully formed six-sided prisms, sometimes of great size. When pure it is perfectly transparent and colorless. Some colored varieties are given special names, as amethyst (violet), rose quartz (pale pink), smoky quartz (black), milky quartz (white). Other varieties of silicon dioxide, some of which also contain water, are chalcedony, onyx, jasper, opal, agate, and flint. Sand and sandstone are largely silicon dioxide.

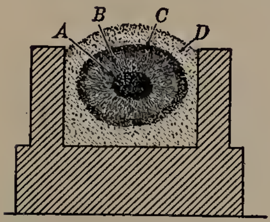


Fig. 146. Cross section of a charged carborundum furnace after being heated

The skeletons of certain microörganisms (infusoria) are composed of nearly pure silica. In some localities these have accumulated in immense deposits, forming a very fine and sharp sand called *infusorial earth.* This material is often used as a scouring powder, especially in scouring soaps.

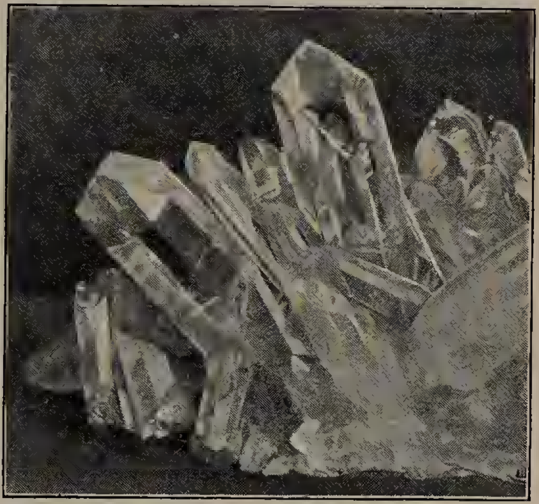


Fig. 147. A cluster of quartz crystals

Properties. As obtained by chemical processes silicon dioxide is an amorphous white powder. In the crystallized state it is very hard and has a density of 2.6. Pure silica begins to soften at about 1600°, and somewhat above this temperature it can be drawn out into threads, blown like glass into tubes and small vessels, and molded into large bowls and pipes for use in chemical industries. These articles are attacked by comparatively few ordinary reagents, and they do not expand or contract to any appreciable extent with even very great changes in temperature. On this account a quartz vessel can be heated red-hot and plunged into cold water without cracking. Fig. 148 shows a quartz crucible and quartz tubes on a wire triangle used to support the crucible when it is heated.

FIG. 148. A crucible and a triangle made from quartz

Chemical conduct. Silica is insoluble in water and in most acids. It is very stable, so that the oxygen which it contains can be removed only by the most powerful reducing agents and at very high temperatures. Hydrofluoric acid attacks it readily (p. 267), according to the equation

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4 + 2\,H_2O$$

Since it is the anhydride of an acid, it dissolves in fused alkalies to form *silicates*. Being nonvolatile, it will drive out most other anhydrides when it is heated with their salts to a high temperature, especially when the silicates so formed are fusible. The following equations illustrate this property:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

Simple silicic acids. Silicon forms two simple acids, *orthosilicic acid* (H_4SiO_4) and *metasilicic acid* (H_2SiO_3). Orthosilicic acid is set free as a jellylike mass when orthosilicates are treated with strong acids. If one attempts to dry this acid, it loses water, passing into metasilicic acid:

$$H_4SiO_4 \longrightarrow H_2SiO_3 + H_2O$$

Metasilicic acid, when heated, breaks up into silica and water, thus:

$$H_2SiO_3 \longrightarrow H_2O + SiO_2$$

Both of these silicic acids are very weak, and their soluble salts are much hydrolyzed in solution.

Salts of silicic acids; silicates. A number of salts of the orthosilicic and metasilicic acids occur in nature. Thus, *mica* ($KAlSiO_4$) is a mixed salt of orthosilicic acid, and *wollastonite* ($CaSiO_3$) is a metasilicate.

Condensed silicic acids. Silicon has the power to form a great many complex acids which may be regarded as derived from the union of several molecules of orthosilicic acid, with the loss of water. These are called *condensed silicic acids.* For example, we have

$$3\,H_4SiO_4 \longrightarrow H_4Si_3O_8 + 4\,H_2O$$

Salts of these condensed acids make up the great bulk of the earth's crust. *Feldspar*, for example, has the formula $KAlSi_3O_8$ and is a mixed salt of the acid $H_4Si_3O_8$, whose formation is represented in the equation above. *Kaolin*, or pure clay, has the formula $H_4Al_2Si_2O_9$ or, as it is commonly written, $Al_2Si_2O_7 \cdot 2\,H_2O$. *Granite* is composed of crystals of feldspar and mica cemented together with amorphous silica.

Water glass. A concentrated solution of sodium silicate (Na_2SiO_3) or of potassium silicate (K_2SiO_3) or of both is called *water glass.* It is a thick, sticky liquid made by fusing sand with the carbonate of sodium or of potassium. It is strongly alkaline in reaction, owing to the ready hydrolysis of these salts. It is used for the purpose of giving a glazed waterproof surface to porous materials, such as wood, stone, and plaster; to render curtains non-inflammable; as a glue for glass and pottery; and as an ingredient in cheap soaps.

Its property of closing pores is turned to account in the preserving of eggs for winter use. The eggs are packed in crocks and then covered with a liquid made by adding 1 volume of commercial water glass to 10 volumes of water. Over the liquid is then poured a little melted paraffin, which soon hardens and excludes the air. Fresh eggs can be preserved for from eight to ten months in this way.

Glass. When sodium silicate, calcium silicate, and silicon dioxide are heated together to a high temperature, the mixture slowly fuses to a transparent liquid, which, on cooling, passes into the rigid material called *glass*. Instead of starting with the silicates of sodium and calcium it is more convenient and economical to heat sodium carbonate (or sulfate) and lime with an excess of clean sand, the silicates being formed during the heating as follows:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

Molding and blowing glass. The way in which the melted mixture is handled in the glass factory depends upon the character of the object to be made. Many articles, such as bottles, are made by blowing the plastic glass into hollow molds of the desired shape. The mold is opened, a lump of plastic glass on a hollow rod is lowered into it, and the mold is then closed. By blowing into the tube the glass is forced into the shape of the mold. The mold is then opened (Fig. 149) and the object lifted out. The top of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now more often made by machinery, in which process the neck is finished first and the bottle then blown by compressed air.

Other objects, such as lamp chimneys, glasses, and beakers, are revolved while being blown in the mold, and have no ridge showing where the mold closes. Window glass is made by gathering a lump of molten glass on the end of a hollow rod (Fig. 150) and blowing this into the form of large hollow cylinders (Fig. 151) about 6 ft. long and 1½ ft. in diameter. These are cut longitudinally (Fig. 152) and are then placed in an oven and heated until they soften, when they are flattened out into plates and cut into the desired sizes. Similar cylinders are now made by dipping a hollow tube into the melted glass and slowly withdrawing it while compressed air is blown through the tube. In this way a very long cylinder is formed. Plate glass is cast into flat slabs (Fig. 153), which are then ground and polished (Fig. 154) to perfectly plane surfaces.


FIG. 149. Making a glass vessel in a mold

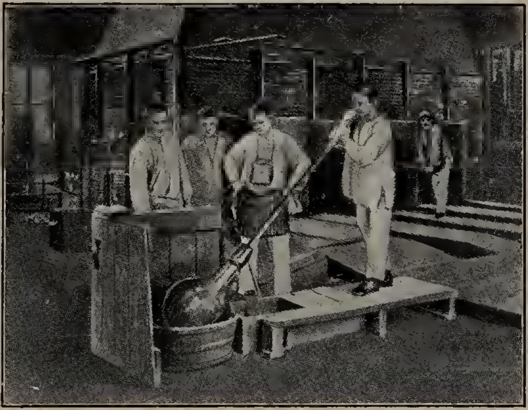


FIG. 150. First step in making window glass: blowing the ball

Varieties of glass. The glass made from sodium carbonate, lime, and sand is soft and easily fusible. If potassium carbonate is substituted for the sodium carbonate, the glass is much harder and less easily fused; increasing the amount of sand has somewhat the same effect.

Potassium glass, of which *Jena* glass is a variety, is largely used in making chemical glassware, because it resists the action of reagents better than the softer sodium glass. If lead oxide is substituted for the whole or a part of the lime, the glass is very soft but has a high index of refraction and is valuable for making optical instruments and artificial jewels (paste).

FIG. 151. Second step in making window glass: blowing the cylinders

Coloring glass. Various substances fused along with the glass impart characteristic colors. The amber color of common bottles is due to iron compounds in the glass; in other cases iron colors the glass green. Cobalt compounds color it deep blue, compounds of manganese give it an amethyst tint, and uranium compounds impart a peculiar yellowish-green color. Iron is nearly always present in sand, and this makes a green glass unless an oxidizing agent is used. The green color is largely removed by the addition of manganese dioxide, which oxidizes the iron compounds to a form having a yellowish tinge, and this color is then neutralized by the manganese, since the yellow produced

FIG. 152. Third step in making window glass: cutting the cylinders

by the iron and the amethyst produced by the manganese are complementary colors, producing white.

Nature of glass. Glass is not a definite chemical compound, and its composition varies between wide limits. Fused glass is really a solution of various silicates, such as those of calcium and lead, in fused sodium silicate or potassium silicate. A certain amount of silicon dioxide is also present. This solution is cooled under such conditions that the dissolved substances do not separate from the solvent. The compounds which are used to color the glass are sometimes converted into silicates which then dissolve in the glass, giving it a uniform color. In other cases, as in the *milky* glasses, which resemble porcelain in appearance, the color or opaqueness is due to the finely divided material evenly distributed throughout the glass, but not dissolved in it. Milky glass is made by mixing calcium fluoride, tin oxide, or some other insoluble substance in the melted glass. Selenium, gold, or cuprous oxide, in very finely divided form scattered through glass, gives it shades of red (ruby glass).


FIG. 153. Casting and rolling plate glass

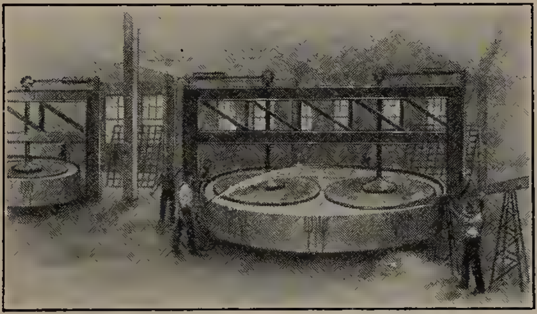


FIG. 154. Polishing plate glass

Enamels. The surface of metal vessels, such as cooking utensils and bathtubs, is often covered by a kind of opaque glass called *enamel* (granite or agate ware). This contains boric oxide (B_2O_3) in place of some silica, and oxides of a number of different metals, such as barium, zinc, or lead, in place of some of the calcium.

TITANIUM

Occurrence. Titanium occurs rather sparingly in nature and is usually found in the form of the dioxide TiO_2, called *rutile*, or as an iron titanite ($FeTiO_3$) known as *ilmenite*, or as a variable constituent of certain magnetic iron ores.

The element. The element can be obtained by the reduction of the dioxide with carbon in an electric furnace, but prepared in this way it always contains carbon and usually nitrogen. Very pure specimens have been prepared by the action of titanium chloride on sodium in a closed steel bomb:

$$TiCl_4 + 4\,Na \longrightarrow Ti + 4\,NaCl$$

When the element contains carbon it is hard and very brittle. Its melting point is above that of platinum, being about 1800°. Its specific gravity is 4.5.

An alloy known as *ferrotitanium* is made by reducing iron ores rich in titanium with carbon. This alloy is manufactured on the large scale at Niagara Falls and is used in preparing titanium steel. It contains 15.5 per cent of titanium, 1.4 per cent of silicon, 7.5 per cent of carbon, and 74.3 per cent of iron.

At high temperatures titanium shows a very marked tendency to unite with nitrogen, the nitride TiN being the product of this direct union. The nitride is therefore always produced in any attempt to prepare titanium in an apparatus to which air has access, and this compound was formerly considered to be the element itself. When iron ores containing titanium are smelted, a substance in appearance resembling crystallized copper is often found in the slag or adhering to the lining of the furnace. This was also at one time supposed to be the metal, but is now known to have the formula $Ti_{10}C_2N_8$.

The compounds. The compounds of titanium very closely resemble those of silicon. The dioxide of titanium, like that of silicon, is an acid anhydride and forms a large number of acids closely resembling the various types of silicic acids. These are even weaker than those of silicon, and their salts hydrolyze more readily. Fluotitanic acid (H_2TiF_6) and its salts are well known.

BORON

Occurrence. Boron occurs in nature as *boric acid* (H_3BO_3) and in salts of *condensed boric acids*, which usually have very complicated formulas.

Preparation and properties. The element boron is extremely difficult to prepare in pure condition, and it is only known in an amorphous state. Its electrical resistance varies to an extraordinary extent with changes in temperature, and this property promises to make it very useful.

Boric acid (H_3BO_3). This compound is found dissolved in the water of hot springs in some localities, particularly in Italy. Being volatile with steam, boric acid is present in the vapor from these springs. The acid is easily obtained from these sources by condensation and evaporation, the necessary heat being supplied by other hot springs.

It is often prepared by treating a strong hot solution of borax ($Na_2B_4O_7$) with sulfuric acid. Boric acid, being but sparingly soluble in water, crystallizes out on cooling:

$$Na_2B_4O_7 + 5\,H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4\,H_3BO_3$$

Boric acid crystallizes in pearly flakes which are slippery to the touch. It is a mild antiseptic and is often used in medicine, particularly for eyewashes. Its acid properties are extremely weak.

Metaboric acid and tetraboric acid. When boric acid is gently heated, it is converted into metaboric acid (HBO_2):

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

On heating metaboric acid to a somewhat higher temperature, *tetraboric acid* ($H_2B_4O_7$) is formed:

$$4\,HBO_2 \longrightarrow H_2B_4O_7 + H_2O$$

FIG. 155. A specimen of the mineral colemanite

Borax. The sodium salt of tetraboric acid has the formula $Na_2B_4O_7$. Borax is a hydrate (p. 251) of this salt and has the formula $Na_2B_4O_7 \cdot 5\,H_2O$ or $Na_2B_4O_7 \cdot 10\,H_2O$ according to the temperature of crystallization. It is found in some arid countries, as southern California and Tibet, but is now made commercially from the mineral *colemanite*. This is the calcium salt of a complex boric acid, $Ca_2B_6O_{11} \cdot 5\,H_2O$, and occurs in large deposits in California. When it is treated with a solution of sodium carbonate, calcium carbonate is precipitated, and borax crystallizes from the solution. Fig. 155 shows a specimen of colemanite.

When heated, borax at first swells up greatly and then melts to a clear glass. This glass has the property of easily dissolving many metallic oxides, and on this account borax is used in brazing for the purpose of removing from the metallic surfaces to be brazed the film of oxide with which they are likely to be covered. These oxides often give a characteristic color to the clear borax glass, and on this account borax beads are often used in testing for the presence of metals.

The reason that metallic oxides dissolve in borax is that borax contains an excess of acid anhydride, as can be more easily seen if its formula is written $2\,NaBO_2 + B_2O_3$. The metallic oxide combines with this excess of acid anhydride, forming a mixed salt of metaboric acid.

Borax is extensively used as a constituent of enamels and glazes for both metal ware and pottery. It is used to soften hard water for domestic purposes, as a mild alkali (like soap), as an antiseptic, and in brazing.

EXERCISES

1. Account for the fact that both silicon and carborundum can be made by heating sand with carbon.

2. Account for the fact that a solution of borax in water is alkaline.

3. What weight of water of hydration does **1** kg. of borax contain?

4. What weight of borax can be made from a ton of colemanite?

5. Why does not sodium silicate form a glass suitable for common use?

6. Calculate the percentage composition of feldspar.

7. Which contains the greater percentage of silicon — feldspar or kaolin?

CHAPTER XXX

THE COLLOIDAL STATE

If to a moderately dilute solution of water glass (sodium silicate) a little sulfuric or hydrochloric acid is added, no very striking change is noticeable. However, if the test tube is set aside for some hours and is then examined, it will be found that the contents of the tube have set to a clear, stiff jelly. This jelly consists essentially of water and silicic acid.

In a similar way a little dried gelatin swells up and dissolves in warm water, but sets to a jelly when the solution is cooled. A great many substances, especially organic materials, assume the jellylike form and have long been called *colloids* — a word that means "glue."

Two states of colloids. We have just seen that the two colloids mentioned are capable of existing in a condition that at first sight appears to be ordinary solution, as well as in the state of jelly. This is not, however, a true solution, but a state of such finely divided material suspended in the solvent that the product closely resembles a solution. That there is a real difference can be shown by the following method:

If a beam of sunlight passes through perfectly clear air, it leaves no path and is invisible; but if it passes through dusty air, it illuminates each dust particle and thus makes a visible path, such as is often seen in a dark room when a sunbeam enters by some crack or hole in a curtain. Now in a perfectly analogous way a beam of light shining through a true solution, such as sodium chloride dissolved in water, leaves no path, because the particles of salt (molecules) are far too small to reflect and scatter light. But when a beam of light passes through the clear silicic acid before it sets to jelly or through the gelatine warmed with water, it leaves a bright path, showing the presence of very small particles in suspension, not in real solution (Fig. 156). This clear solution-like condition is called a *sol* (or sometimes *hydrosol*), while the jellylike state is called a *gel* (or *hydrogel*). Many substances can exist as either sol or gel, and in either state are called *colloids*.

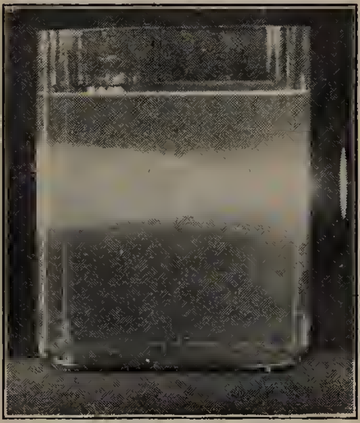


FIG. 156. A beam of light shining through a colloidal solution

Coagulation of colloids. The changing of a sol into a gel is called *coagulation*. The white of an egg, beaten up with water, constitutes a typical sol. When this is heated the sol turns into an opaque white gel that will not again pass into the sol form. In other words the coagulation is irreversible. In the case of gelatine, cooling produces the gel and heating produces the sol, and the coagulation can be reversed as often as may be desired.

Sometimes the addition of an electrolyte (acid, base, salt) occasions coagulation, as in the example of the sol of silicic acid. Plastic clay well stirred with water is partly material that can be filtered off (suspended matter) and partly material that is too finely divided to be filtered (sol). The addition of a few drops of sulfuric acid quickly precipitates the sol as gel, and so too does the addition of certain salts. Alkalies tend to make the sol condition more stable and may even cause the coagulated gel to pass again into the sol form. Sometimes the addition of one sol to another causes the coagulation of both as gel, while in other cases the sol state is rendered more stable. For example, when colloidal ferric hydroxide is added to colloidal antimony sulfide or colloidal arsenious oxide, both are precipitated. On the other hand, gelatin renders many sols more stable.

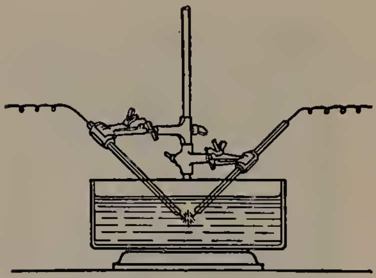


FIG. 157. The preparation of metallic colloids by sparking under water

Preparation of colloidal sols. In a general way it may be said that colloidal sols may be produced in either of two ways:

1. *By powdering solids.* We may start with a solid and by mechanical means powder it until it is so finely divided that it will make a sol when mixed with water. In the case of metals and some other substances this may be done by dipping electrodes made of the substance under water and causing a strong electric current to strike an arc between the electrodes (Fig. 157). Particles of the electrode are torn off by the current and remain suspended in the water as sol. The sols of gold are purple, blue, or green in color, depending upon the size of the particles. Those of platinum are brown.

2. *By imperfect precipitation.* When two substances are brought together that are capable of forming an insoluble precipitate, in general we expect the precipitate to form. Under certain circumstances, especially if the solutions are very dilute, precipitation does not take place but the

expected insoluble precipitate remains suspended as sol. Thus, when chromium chloride or chromium sulfate is treated with sodium hydroxide we expect the precipitation of insoluble chromium hydroxide:

$$CrCl_3 + 3\,NaOH \longrightarrow Cr(OH)_3 + 3\,NaCl$$

If the solutions are cold and are brought together slowly, no precipitate forms; but after a time the contents of the test tube sets to a jelly. In a similar way nearly any insoluble material may be obtained either as a sol or a gel, though very strongly crystalline substances, such as barium sulfate ($BaSO_4$), are difficult to obtain in these forms.

Colloids and hydrolysis. We have seen that salts of a weak acid or a weak base undergo some hydrolysis in solution (p. 226). In many cases either the acid or the base is known to be insoluble, yet precipitation does not always occur; so we are forced to assume the presence *in solution* of a compound we know to be insoluble.

Thus, sodium silicate is markedly hydrolized, as is shown by its strongly alkaline reaction, and silicic acid must be produced in the reaction. We know it to be insoluble, yet no precipitate forms when sodium silicate is dissolved in water. As another example we may take the violet-colored salt ferric nitrate, $Fe(NO_3)_3 \cdot 6\,H_2O$. If a crystal of this salt is placed in water, it forms a yellow or brown solution that is strongly acid in reaction, indicating considerable hydrolysis. Ferric hydroxide, which should be formed in the reaction, is highly insoluble and should therefore form as a precipitate, but does not.

These apparently contradictory facts may be reconciled if we suppose that the silicic acid and the ferric hydroxide remain as colloidal sols instead of separating as gels or precipitates. Examination by transmitted light shows that this explanation is warranted by the appearance of the hydrolized solutions.

Nature of colloids. From what has been said it will be seen that colloids are not a special kind of substance, but that the colloidal condition is one which any substance may assume just as it may occur as a solid, as a liquid, as a gas, or in true solution. In this state it is too coarsely divided to be a true solution, yet too finely divided to be removed by filtration or settling. It will also be apparent that there can be no very sharp distinction drawn between a colloid and a fine suspension, the one passing by imperceptible stages into the other.

It is probable that each particle of a typical colloid consists of thousands of molecules, but that these are clumped together without any special order. When the particles assume an orderly arrangement they constitute *crystals*, and crystalline particles continue to grow in size, precipitating from the solution in definite solid form. On the other hand, the colloid clumps tend to form networks or spongelike forms that inclose water and constitute jellies.

Colloids and the industries. Many important industries depend upon the properties of colloids. Many colored glasses, such as ruby glass, owe their color to colloidal material dispersed through the glass. Photographic plates are made of colloidal salts of silver dispersed through gelatin or some similar substance. Pastes of various kinds, bread dough, glues, and cements owe many of their properties to their colloidal character. Soils contain a great deal of colloidal material, both organic and mineral, and their ability to hold water and to support the growth of plants is greatly dependent upon this fact. Rubber is a typical colloid, as are other similar plastic materials, such as gums and waxes. Many minerals have originated from the gradual hardening of gels and owe their peculiar structure to this origin, as, for example, the banded structure of onyx and agate. Indeed, we are just beginning to realize how much of the chemistry of everyday life is in the realm of colloidal materials.

Emulsions. If water and a little kerosene are vigorously shaken together, the resulting liquid is milky in appearance and consists of very small drops of kerosene scattered through the water. These drops rapidly run together and collect into a layer of oil floating on the water, and the milky appearance entirely vanishes. If the experiment is repeated, but with the addition of a very small particle of soap before the shaking, the product remains milky for a long time (Fig. 158). Indeed, it may remain so for months. Such a milky liquid is called an *emulsion.* Under other conditions water and kerosene produce an emulsion which consists of droplets of water dispersed in kerosene. Milk is a natural emulsion, but not a very perfect one, for the cream rises to the top rather rapidly.

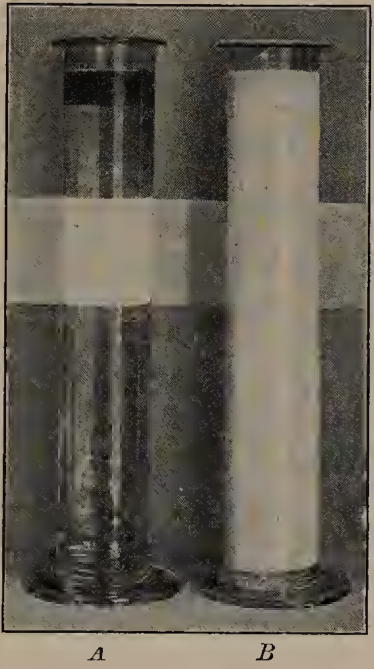


FIG. 158. Emulsions

In *A* the oil floats on the water; in *B* an emulsion has been formed by adding soap

It will be seen that the essential distinction between a colloid and an emulsion is that in the first case the particles are those of a solid, while in the case of an emulsion they are liquid drops. We may expect any one liquid to form an emulsion with any other, provided the two do not mix to form a solution as do water and alcohol. For an emulsion to be at all stable it appears to be necessary that a third colloidal substance should be present, such as the soap in the experiment with kerosene, or the casein of milk.

Fogs. If the air is perfectly free from solid particles, it may become greatly supersaturated with water vapor. If now dust or smoke mingles with the supersaturated air, each little dust particle becomes a center upon which water vapor condenses, and since the solid particles are very numerous, the water droplets are also very numerous and very small. The result of such condensation is what we call a fog. It will be seen that it is but natural that large cities, especially those situated near large bodies of water or rivers and in humid regions, should be subject to fog. From a chemical standpoint a fog might be considered as an emulsion in which the water droplets are dispersed through a gas instead of through another liquid.

CHAPTER XXXI

THE METALS

The metals. The elements so far considered have nearly all been those whose compounds with oxygen and hydrogen are *acids*, and they are called the *acid-forming* elements or the nonmetals. Those which we shall now study are known collectively as the *metals.* The hydroxides of the metals are *bases*, and on this account the *metals are sometimes defined as those elements whose hydroxides are bases.* When the hydroxide of a metal or any of the simple salts derived from the hydroxide are dissolved in water, the metallic element forms the cation and carries a positive charge.

The distinction between a metal and a nonmetal is not a very sharp one, since the hydroxides of a number of elements act as bases under some conditions and as acids under others. We have seen that antimony is an element of this kind.

Properties of the metals. The metals are all solids except mercury, which is a liquid. Most metals have a high density, although three of them, namely, lithium, sodium, and potassium, are lighter than water. As a rule, the metals are good conductors of heat and electricity, are notably crystalline in structure, and take a bright polish. With the exception of gold and copper, they have a silvery luster. Most of them combine readily with oxygen and sulfur, and their surfaces quickly tarnish on exposure to the air. A few of them, such as gold and platinum, have little chemical activity and so retain their luster in the air.

Occurrence of metals in nature. A few of the metals are found in nature in the free state. Among these are gold, platinum, and frequently copper. They are usually found combined with other elements in the form of oxides or salts of various acids. Silicates, carbonates, sulfides, and sulfates are the most abundant of these salts. All inorganic substances occurring in nature, whether they contain a metal or not, are called *minerals*. Those minerals from which a useful substance can be extracted are called *ores* of the substance.

Extraction of metals: metallurgy. The process of extracting a metal from its ores is called the *metallurgy* of the metal. The metallurgy of each metal presents peculiarities of its own, but there are several methods of general application which are very frequently employed.

1. ***Reduction of an oxide with carbon.*** Many of the metals occur in nature in the form of oxides. When some of these oxides are heated to a high temperature with carbon, the oxygen combines with the carbon and the metal is set free. Iron, for example, occurs largely in the form of the oxide Fe_2O_3. When this is heated with carbon the reaction expressed in the following equation takes place:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$

Many ores other than oxides may be changed into oxides which can then be reduced by carbon. The conversion of such ores into oxides is generally accomplished by heating, and the process is called *roasting*. Many carbonates and hydroxides decompose directly into the oxide on being heated. Sulfides, on the other hand, must be heated in a current of air, the oxygen of the air entering into the reaction. The following equations will serve to illustrate these changes in the case of the ores of iron:

$$FeCO_3 \longrightarrow FeO + CO_2$$
$$2\,Fe(OH)_2 \longrightarrow Fe_2O_3 + 3\,H_2O$$
$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$

2. ***Reduction of an oxide with aluminium.*** Not all oxides, however, can be reduced by carbon. In such cases aluminium may be used. Thus, chromium may be obtained in accordance with the following equation:

$$Cr_2O_3 + 2\,Al \longrightarrow 2\,Cr + Al_2O_3$$

This method was first used by the German chemist Goldschmidt and is called the Goldschmidt method.

3. ***Electrolysis.*** In recent years increasing use is being made of the electric current in the preparation of metals. In some cases the separation of the metal from its compounds is accomplished by passing the current through a solution of a suitable salt of the metal, the metal usually being deposited upon the cathode. In other cases the current is passed through a fused salt of the metal, the chloride being best adapted to this purpose.

Electrochemical industries. Most of the electrochemical industries of the country are carried on where water power is abundant, since this furnishes the cheapest means for the generation of electrical energy. Niagara Falls is the most important locality in this country for such industries, and many different electrochemical products are manufactured there (Fig. 159). Some industries depend upon electrolytic processes, while in others the electrical energy is used merely as a source of heat. In the latter case the process is called *thermoelectric.*

Preparation of compounds of the metals. Since the compounds of the metals are so numerous and so varied in character, there are many ways of preparing them. In many cases the properties of the substance to be prepared, or the material available for its preparation, suggest a rather unusual way. There are, however, a number of general principles which are constantly applied in the preparation of the compounds of the metals, and a clear understanding of them will save much time and effort in remembering the details in any given case. Some of the general methods for the preparation of compounds are the following:

FIG. 159. Electrochemical power plants at Niagara Falls

1. *By direct union of two elements.* This is usually accomplished by heating the two elements together. Thus, the sulfides, chlorides, and oxides of a metal can generally be obtained in this way. The following equations serve as examples of this method:

$$Fe + S \longrightarrow FeS$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

2. ***By the decomposition of a compound.*** This decomposition may be brought about either by heat alone or by the combined action of heat and a reducing agent. Thus, when the nitrate of a metal is heated the oxide of the metal is usually obtained. Copper nitrate, for example, decomposes as follows:

$$2\,Cu(NO_3)_2 \longrightarrow 2\,CuO + 4\,NO_2 + O_2$$

Similarly, the carbonates of the metals yield oxides, thus:

$$CaCO_3 \longrightarrow CaO + CO_2$$

Most of the hydroxides form an oxide and water when heated:

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O$$

When heated with carbon, sulfates are reduced to sulfides, thus:

$$BaSO_4 + 2\,C \longrightarrow BaS + 2\,CO_2$$

3. ***Methods based on equilibrium in solution.*** In the preparation of compounds the first requisite is that the reactions chosen shall be of such a kind as will go on to completion. In the chapter on chemical equilibrium (p. 224) it was shown that reactions in solution may become complete in either of three ways: (1) a gas may be formed which escapes from solution; (2) an insoluble solid may be formed which precipitates; (3) two different ions may combine to form undissociated molecules. By the judicious selection of materials these principles may be applied to the preparation of a great variety of compounds, and illustrations of such methods will very frequently be found in the subsequent pages.

4. ***By fusion methods.*** It sometimes happens that substances which are insoluble in water and in acids, and which cannot therefore be brought into double decomposition in the usual way, are soluble in other liquids, and

when dissolved in them can be decomposed and converted into other desired compounds. Thus, barium sulfate is not soluble in water, and sulfuric acid, being less volatile than most other acids, cannot easily be driven out from this salt. When brought into contact with melted sodium carbonate, however, it dissolves in it and, since barium carbonate is insoluble in melted sodium carbonate, double decomposition takes place:

$$Na_2CO_3 + BaSO_4 \longrightarrow BaCO_3 + Na_2SO_4$$

When the cooled mixture is dissolved in water the sodium sulfate formed in the reaction, together with any excess of sodium carbonate which may be present, dissolves. The barium carbonate can then be filtered off and converted into any desired salt by the processes already described.

Important insoluble compounds. Since precipitates play so important a part in the reactions which substances undergo, as well as in the preparation of many chemical compounds, it is important to know what substances are insoluble in water. Knowing this, we can in many cases predict reactions under certain conditions, and are assisted in devising ways to prepare desired compounds. While there is no general rule which will enable one to foretell the solubility of any given compound, nevertheless a few general statements can be made which will be of much assistance.

1. ***Hydroxides.*** All hydroxides are insoluble in water save those of ammonium, sodium, potassium, calcium, barium, and strontium.

2. ***Nitrates.*** All nitrates are soluble in water.

3. ***Chlorides.*** All chlorides are soluble in water save silver and mercurous chlorides. (Lead chloride is but slightly soluble.)

4. ***Sulfates.*** All sulfates are soluble in water save those of barium, strontium, and lead. (Sulfates of silver and calcium are only moderately soluble.)

5. ***Sulfides.*** All sulfides are insoluble in water save those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are insoluble in water, but are changed by hydrolysis into acid sulfides which are soluble; on this account they cannot be prepared by precipitation.

6. ***Carbonates, phosphates, and silicates.*** All normal carbonates, phosphates, and silicates are insoluble in water save those of ammonium, sodium, and potassium.

EXERCISES

1. Write equations representing four different ways for preparing $Cu(NO_3)_2$.

2. Write equations representing six different ways for preparing $ZnSO_4$.

3. Write equations for two reactions to illustrate each of the three ways in which reactions in solutions may become complete.

4. Give one or more methods for preparing each of the following compounds: $CaCl_2$, $PbCl_2$, $BaSO_4$, $CaCO_3$, $(NH_4)_2S$, Ag_2S, PbO, $Cu(OH)_2$ (for solubilities, see last paragraph of chapter). State in each case the general principle involved in the method of preparation chosen.

CHAPTER XXXII

THE ALKALI METALS

Metal	Atomic weight	Density	Melting point	First prepared
Lithium (Li) . . .	6.94	0.534	186.0°	Arfvedson, 1817
Sodium (Na) . . .	23.00	0.971	97.5°	Davy, 1807
Potassium (K) . .	39.10	0.862	62.3°	Davy, 1807
Rubidium (Rb) . .	85.45	1.532	38.0°	Bunsen, 1861
Cæsium (Cs) . . .	132.81	1.87	26.4°	Bunsen, 1860

Characteristics of the family. The elements listed in the above table constitute a family in Group I of the periodic table. They are called the alkali metals for the reason that the most familiar members of the family, namely, sodium and potassium, are constituents of compounds that have long been known as alkalies. Before considering each element separately it is advisable to discuss briefly the family as a whole since a number of statements can be made that apply to all of these elements.

1. ***Occurrence.*** While none of these metals occur free in nature, their compounds are widely distributed, being found in sea and mineral waters, in salt beds, and in many rocks. Sodium and potassium are, however, the only ones that occur in abundance.

2. ***Preparation.*** The alkali metals are most readily prepared by the electrolysis of their fused hydroxides or chlorides. They may also be prepared by the reduction of their oxides, hydroxides, or carbonates.

3. ***Properties.*** They are soft metals, easily molded by the fingers. They have low melting points and small densities, as shown in the table. Their densities (sodium excepted) are in the same order as their atomic weights, while their melting points and boiling points are in the reverse order. The pure metals have a silvery luster, but tarnish at once when exposed to the air, because of the formation of a film of oxide upon their surface; hence they are often preserved in some liquid, such as kerosene, which contains no oxygen. They stand at the head of the electrochemical series of the metals (p. 191) and in general are very active elements.

FIG. 160. Robert Wilhelm Bunsen (1811–1899)

A distinguished German chemist who discovered rubidium and cæsium, invented the spectroscope and the laboratory burner, and contributed to many advances in chemistry

4. ***Compounds.*** The alkali metals act as univalent elements in the formation of compounds. Their hydroxides (MOH) are white solids and are very soluble in water. In dilute aqueous solutions these hydroxides are largely ionized and to about the same extent, forming the ions M^+ and OH^-; hence their solutions are strongly basic. With few exceptions the salts of the alkali metals are white solids, and, unless otherwise stated, it will be so understood in the description of the individual compounds. With the exception of lithium these metals form very few

insoluble compounds, so that it is difficult to prepare their compounds by precipitation. The compounds of sodium and potassium are so similar in properties that for most purposes they can be used interchangeably. Those of sodium are cheaper than the corresponding compounds of potassium and so are more largely used.

Sodium and potassium are the only important members of the family. Sodium, as well as its hydroxide, has been described in Chapter XV, and this description should be carefully reviewed in connection with the present chapter.

Compounds of Sodium

General. In addition to sodium hydroxide (p. 175) sodium forms a large number of compounds. With the exception of the nitrate all these compounds are prepared from the chloride, since it is so abundant and inexpensive. The processes involved are often complicated, owing to the fact that the compounds of sodium are all soluble and therefore cannot be prepared directly from the chloride by precipitation; moreover, the chloride is a salt of a strong acid and is not readily acted upon by most other acids. Experiments have shown that the most economical method of procedure consists either in first changing the chloride into the hydroxide by the electrolysis of its aqueous solution or in converting it into the carbonate by the methods to be described. Since the hydroxide is a base and the carbonate is a salt of a very volatile acid, both are readily changed into other compounds.

Sodium peroxide (Na_2O_2). Since sodium is a univalent element, we should expect it to form an oxide of the formula Na_2O. While such an oxide can be prepared, the peroxide, Na_2O_2, is much better known. It is a yellowish-white powder made by burning sodium in air. Its chief use is as an oxidizing agent. When heated with oxidizable substances it gives up a part of its oxygen, as shown in the equation

$$2\,Na_2O_2 \longrightarrow 2\,Na_2O + O_2$$

Water decomposes it in accordance with the equation

$$Na_2O_2 + 2\,H_2O \longrightarrow 2\,NaOH + H_2O_2$$

Acids act readily upon it, forming a sodium salt and hydrogen peroxide:

$$Na_2O_2 + 2\,HCl \longrightarrow 2\,NaCl + H_2O_2$$

In these last two reactions the hydrogen dioxide formed decomposes into water and oxygen unless precautions are taken to prevent the temperature from rising (p. 27):

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Sodium chloride (common salt) (NaCl). Sodium chloride, or common salt, is very widely distributed in nature. Thick strata, evidently deposited by the evaporation of salt water, are found in many places. In the United States the most important localities for salt are New York, Michigan, Ohio, and Kansas. Sometimes the salt is mined, especially if it is in the pure form called *rock salt.* More frequently a strong brine is pumped from deep wells sunk into the salt deposit. The brine is evaporated either by heating or, in the preparation of the coarser grades of salt, by simply exposing the brine to the air (Fig. 161). Salt crystallizes in the form of small cubes.

Uses of salt. Since salt is so abundant in nature, it is used in the preparation of nearly all compounds containing either sodium or chlorine. These include many substances of the highest importance to civilization, such as soap, glass, hydrochloric acid, soda, and bleaching powder. Enormous quantities of salt are therefore produced each year. Small quantities are essential to the life of man and animals. Pure salt does not absorb moisture; the fact that ordinary salt becomes moist when exposed to air is not due to a property of the salt but to impurities occurring in it, especially to the presence of calcium and magnesium chlorides.

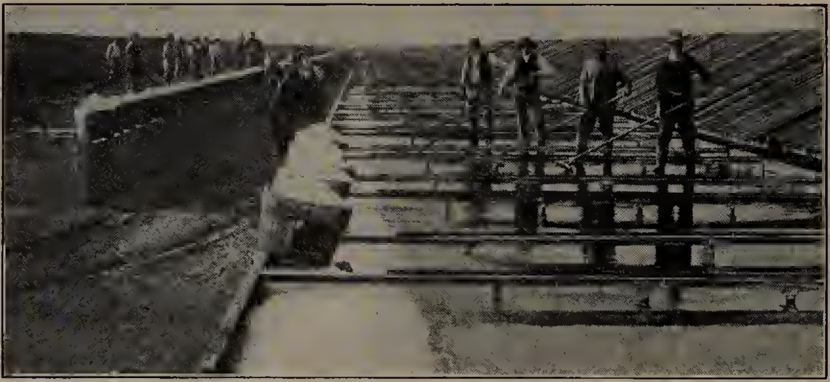


FIG. 161. The evaporation of salt brine in the open air

Sodium bromide ($NaBr$); sodium iodide (NaI). These compounds resemble sodium chloride in their physical properties. They can be prepared by the action of bromine and iodine respectively upon a solution of sodium hydroxide (p. 409). They are used to a limited extent in photography and in medicines.

Sodium sulfate (Na_2SO_4). This salt is prepared by the action of sulfuric acid upon sodium chloride, hydrogen chloride being formed at the same time (p. 167):

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

It is also prepared by the action of sodium chloride upon magnesium sulfate, the latter being obtained in large quantities in the manufacture of potassium chloride:

$$MgSO_4 + 2\,NaCl \longrightarrow Na_2SO_4 + MgCl_2$$

The anhydrous sodium sulfate is a white solid. It is readily soluble in water and, under ordinary conditions, crystallizes out as the hydrate, $Na_2SO_4 \cdot 10\,H_2O$ (known as *Glauber's salt*). Large quantities of sodium sulfate are used in making sodium carbonate and glass. The salt is also used in medicine.

Sulfites of sodium. The acid sulfite, $NaHSO_3$, often called sodium bisulfite, is formed by saturating a solution of sodium carbonate with sulfur dioxide. Sulfurous acid is first formed by the union of the dioxide with water, and this decomposes the carbonate:

$$Na_2CO_3 + 2\,H_2SO_3 \longrightarrow 2\,NaHSO_3 + CO_2 + H_2O$$

The normal sulfite, Na_2SO_3, is prepared by adding sodium carbonate to a saturated solution of the acid sulfite in the proportion indicated in the following equation:

$$2\,NaHSO_3 + Na_2CO_3 \longrightarrow 2\,Na_2SO_3 + H_2O + CO_2$$

Both of the sulfites of sodium readily absorb oxygen, forming the corresponding sulfates; they are therefore reducing agents. They are used to some extent as bleaching agents and as preservatives.

Sodium thiosulfate ($Na_2S_2O_3$). This salt is made by boiling a solution of sodium sulfite with sulfur:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

The hydrate, $Na_2S_2O_3 \cdot 5\,H_2O$, is frequently called *sodium hyposulfite*, or simply *hypo*. It is used in photography and in the bleaching industry to absorb the excess of chlorine which is left upon the bleached fabrics.

Sodium carbonate (Na_2CO_3). There are two different methods now employed in the manufacture of this salt.

1. ***Leblanc process.*** This older process involves several distinct reactions, as shown in the following equations:

(*a*) Sodium chloride is first converted into sodium sulfate:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

(*b*) The sodium sulfate is next reduced to sodium sulfide by heating it with carbon:

$$Na_2SO_4 + 2\,C \longrightarrow Na_2S + 2\,CO_2$$

(*c*) The sodium sulfide is then heated with calcium carbonate, when the following reaction takes place:

$$Na_2S + CaCO_3 \longrightarrow CaS + Na_2CO_3$$

2. ***Solvay process.*** This more modern process depends upon reactions taking place *in solution* and represented in the equations

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl \qquad (1)$$
$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (2)$$

When concentrated solutions of sodium chloride and of ammonium hydrogen carbonate are brought together, the sparingly soluble sodium hydrogen carbonate is precipitated as represented in equation (1). This, by heating, is converted into the normal carbonate as indicated in equation (2). The ammonium chloride formed (equation (1)) is treated with lime (p. 202), ammonia being liberated. This ammonia together with water and the carbon dioxide generated as indicated in equation (2) combine to form ammonium hydrogen carbonate:

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$

This is treated with salt, and the process is begun over again, according to equation (1).

Historical. In former times sodium carbonate was made by burning seaweeds and extracting the carbonate from their ash.

On this account the salt was called *soda ash*, and the name is still in common use. During the French Revolution this supply was cut off, and in behalf of the French government Leblanc (Fig. 162) made a study of methods of preparing the carbonate directly from common salt. As a result he devised the method which bears his name and which was used exclusively for many years. Although the method is still used in England, it has been entirely replaced in the United States by the Solvay process, which was devised by the Belgian chemist Solvay in 1863.

FIG. 162. Nicolas Leblanc (1742–1806)

Inventor of the first method of preparing sodium carbonate from salt. (Statue erected in Paris)

By-products. The substances obtained in a given process, aside from the main product, are called the *by-products*. The success of many processes depends upon the value of the by-products formed. Thus, hydrochloric acid, a by-product in the Leblanc process, is valuable enough to make the process pay, even though sodium carbonate can be made more cheaply in other ways.

Properties of sodium carbonate. Sodium carbonate forms large crystals of the formula $Na_2CO_3 \cdot 10\,H_2O$, known as *washing soda*, or *sal soda*. The monohydrate, $Na_2CO_3 \cdot H_2O$, is also prepared and used commercially to some extent.

An aqueous solution of sodium carbonate has a mild alkaline reaction and is used for laundry purposes. Mere mention of the fact that the salt is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. It is one of the few soluble carbonates.

Sodium hydrogen carbonate ($NaHCO_3$). This salt, called *bicarbonate of soda*, or *baking soda*, is made by the Solvay process, as explained above, or by passing carbon dioxide into concentrated solutions of sodium carbonate:

FIG. 163. A deposit of sodium nitrate in Chile

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\,NaHCO_3$$

It is an essential constituent of all baking powders.

Sodium nitrate ($NaNO_3$). This substance, known also as *Chile saltpeter*, is found in nature in certain arid regions, where apparently it has been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile, and most of the nitrate of commerce comes from that country. Fig. 163 shows a deposit of sodium nitrate in Chile after it has been broken apart by explosives. The commercial salt is prepared by dissolving the crude nitrate (known as *caliche*) in water, allowing the insoluble earthy materials to settle, and evaporating to crystallization the clear solution so obtained. The soluble impurities remain for the most part in the mother liquors.

Since this salt is the only nitrate found extensively in nature, it is the material from which other nitrates, and also nitric acid, are prepared. Enormous quantities are used as a fertilizer and in the manufacture of sulfuric acid.

Sodium cyanide (NaCN). This salt of hydrocyanic acid readily dissolves gold and is used for extracting this metal when it is scattered in small quantities through earthy material. It is prepared chiefly by heating a mixture of carbon and sodamide ($NaNH_2$), the latter compound being obtained by the action of sodium upon ammonia:

$$2\,Na + 2\,NH_3 \longrightarrow 2\,NaNH_2 + H_2$$
$$NaNH_2 + C \longrightarrow NaCN + H_2$$

Sodium cyanide is a white solid. Its aqueous solution is strongly alkaline. The compound is not only extremely poisonous, but in contact with acids evolves the very poisonous hydrocyanic acid (HCN).

The phosphates of sodium. Sodium forms three salts with phosphoric acid, one normal and two acid salts. The most common of these is disodium phosphate, Na_2HPO_4. It is prepared by the action of phosphoric acid upon sodium carbonate:

$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + H_2O + CO_2$$

This salt crystallizes as the hydrate, $Na_2HPO_4 \cdot 12\,H_2O$. It is a constituent of the human organism.

The normal phosphate, Na_3PO_4, is readily soluble in water and forms a strongly alkaline solution due to partial hydrolysis:

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH$$

Sodium hypochlorite (NaClO). This salt is prepared by electrolyzing a solution of sodium chloride under such conditions that the chlorine and sodium hydroxide generated in the process of electrolysis react to form sodium hypochlorite as explained on page 276. The equation for the reaction is as follows:

$$2\,NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O$$

The salt is unstable and is obtained only in dilute solution. This solution (called the Carrel-Dakin solution) is used as an antiseptic in the treatment of wounds.

Sodium chlorate ($NaClO_3$). This salt of chloric acid is formed according to the general method for preparing chlorates (p. 276). When heated it breaks down into sodium chloride and oxygen, resembling potassium chlorate in this respect (p. 25). It is an excellent oxidizing agent and is used in the manufacture of fireworks and munitions.

POTASSIUM

Occurrence. Potassium is a rather abundant element, being a constituent of many igneous rocks, such as the feldspars and micas. Very large deposits of the chloride and the sulfate, associated with compounds of calcium and magnesium, are found at Stassfurt, Germany, and are known as the *Stassfurt salts.*

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. Its soluble compounds are absorbed by growing plants and built up into complex vegetable tissues; when these are burned, the potassium remains in the ash in the form of carbonate. The crude carbonate can be separated from wood ashes by dissolving it in water. This was formerly the chief source of potassium compounds, but they are now prepared mostly from the salts of the Stassfurt deposits.

Stassfurt salts. These salts, evidently deposited from sea water under peculiar geological conditions, form very extensive deposits in middle and north Germany, the most noted locality for working them being at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. Over thirty different minerals are present, although some in very small quantities. Fig. 164 shows a cross section of these deposits. While from a chemical standpoint these strata are salts, they are as solid and hard as many kinds of stone and are mined as stone or coal would be. Since the strata differ in general appearance, each can be mined separately, and the various minerals can be worked up by methods adapted to each particular case. The chief minerals of commercial importance in these deposits are the following:

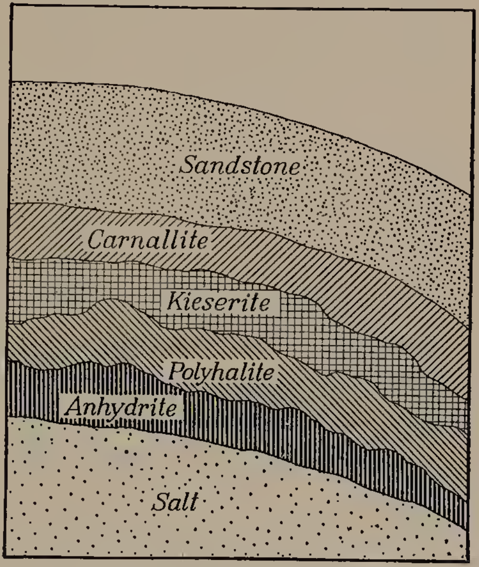


Fig. 164. Cross-section diagram of the Stassfurt salt deposits

Sylvite	KCl
Anhydrite	$CaSO_4$
Carnallite	$KCl \cdot MgCl_2 \cdot 6\,H_2O$
Kainite	$MgSO_4 \cdot KCl \cdot 3\,H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Schönite	$K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O$

Other sources of potassium. The potassium compounds are of great value, especially in the manufacture of fertilizers. The importance of the United States having its own source of these compounds was made evident during the great war, when the supply from the Stassfurt salts was cut off. The common feldspar which is so abundant in the earth's crust contains potassium, but no economical method has been found as yet for changing this into the desired compounds, such as potassium chloride or potassium sulfate. While sodium rather than potassium is likely to be present in sea plants, nevertheless some of these plants, such as the giant algæ of the California coast, contain potassium chloride, amounting in some cases to 30 per cent of their dry weight; indeed, the dried algæ are being used to some extent as a fertilizer. An effort has also been made to obtain the salts from the complex mineral alunite ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4\,Al(OH)_3$), considerable deposits of which are found in Utah. No satisfactory source, however, has as yet been found that is at all comparable with the Stassfurt deposits.

Preparation and properties. Potassium is prepared by methods similar to those used in the preparation of sodium. It is more active than sodium; otherwise the properties of the two metals are alike.

Potassium hydroxide (caustic potash) (KOH). Potassium hydroxide is prepared by methods exactly similar to those used in the preparation of sodium hydroxide, which compound it closely resembles in both physical and chemical properties. It is not used to any very great extent, being replaced by the cheaper sodium hydroxide.

Action of the halogen elements on bases. We have seen that when chlorine is passed into a solution of potassium hydroxide a reaction takes place (p. 276) and that the nature of the reaction varies according to the temperature of the solution. If the solution is cold, potassium hypochlorite and potassium chloride are formed, according to the following equation:

$$2\,KOH + Cl_2 \longrightarrow KClO + KCl + H_2O$$

If the solution is hot, however, potassium chlorate and potassium chloride are formed:

$$6\,KOH + 3\,Cl_2 \longrightarrow KClO_3 + 5\,KCl + 3\,H_2O$$

This reaction is a general one between the halogen elements and the soluble bases. Thus, in place of chlorine in the above equations, one may substitute bromine or iodine; also in place of the potassium hydroxide one may substitute sodium hydroxide or calcium hydroxide. It is possible by this reaction to prepare a number of important compounds. It does not follow, however, that this method of preparation of any particular compound is necessarily the most economical one.

Potassium halides. Of these compounds *potassium chloride* is the most familiar, since it is found in such large quantities in the Stassfurt deposits. The mineral sylvite is nearly pure potassium chloride. The salt is obtained not only from sylvite but also from carnallite. In its general properties potassium chloride resembles sodium chloride. It is used in the preparation of nearly all other potassium salts and as a fertilizer. *Potassium bromide* (KBr) is prepared by the action of bromine upon a hot solution of potassium hydroxide (see preceding paragraph). *Potassium iodide* (KI) is prepared by the same methods as those used in preparing potassium bromide, with the substitution of iodine for bromine. Both the iodide and the bromide are used in photography and in medicine.

Potassium chlorate ($KClO_3$). This compound is similar in properties to sodium chlorate (p. 406) and is prepared by the same general methods. It is an excellent oxidizing agent and, like sodium chlorate, is used in the manufacture of munitions, fireworks, and matches; indeed, it is preferred to sodium chlorate, since the latter compound tends to absorb moisture from the air.

Potassium nitrate (saltpeter) (KNO_3). This salt is found native in some regions where the climate is hot and dry, being formed by the decay of nitrogenous organic matter in the presence of earthy material containing potassium. Saltpeter was formerly made by imitating these conditions. It is now prepared by the action of sodium nitrate upon potassium chloride (the former compound being obtained from Chile and the latter from the Stassfurt deposits):

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

The reaction depends for its success upon the apparently insignificant fact that sodium chloride is almost equally soluble in cold and in hot water. All four compounds represented in the equation are rather soluble in cold water, but in hot water sodium chloride is far less soluble than the other three. When hot saturated solutions of sodium nitrate and potassium chloride are brought together sodium chloride precipitates and can be filtered off, leaving potassium nitrate in solution together with some sodium chloride. When the solution is cooled, potassium nitrate crystallizes out, leaving small amounts of the other salts in solution.

Potassium nitrate is an excellent oxidizing agent, and its chief use is in the manufacture of gunpowder. For this purpose it is preferable to sodium nitrate, since the latter tends to absorb moisture, and powder made from it, if exposed to air, soon becomes moist and unfit for use. Small amounts of the nitrate are also used in medicine and as a preservative for meats, especially for corned beef.

Potassium carbonate (K_2CO_3). This compound can be prepared from potassium chloride by the Leblanc process, just as sodium carbonate is prepared from sodium chloride. Commercially it is prepared chiefly according to the reactions indicated in the following equations:

$$3\,MgCO_3 + 2\,KCl + CO_2 + H_2O \longrightarrow 2\,MgKH(CO_3)_2 + MgCl_2$$

$$2\,MgKH(CO_3)_2 \longrightarrow 2\,MgCO_3 + K_2CO_3 + CO_2 + H_2O$$

Potassium carbonate is used in the manufacture of glass. When carbon dioxide is passed into an aqueous solution of potassium carbonate, potassium bicarbonate ($KHCO_3$) is formed.

Other salts of potassium. Among the other salts of potassium frequently met with are the sulfate, K_2SO_4; the acid sulfate, $KHSO_4$; the acid sulfite, $KHSO_3$; and the cyanide, KCN. They are all white solids and closely resemble the corresponding sodium compounds.

Deliquescence. A large number of salts resemble sodium nitrate in their tendency to absorb moisture from the air. If the process continues long enough, the salt may pass into solution in the water absorbed. Such a salt is said to be *deliquescent*, and all very soluble salts are deliquescent. Common salt is not itself deliquescent, but it usually contains enough deliquescent salts of calcium and magnesium to cause it to become moist in wet weather.

Lithium, Rubidium, Cæsium

Of the three remaining elements of the family — lithium, rubidium, and cæsium — lithium is by far the most common, the other two being very rare. Lithium chloride and lithium carbonate are not infrequently found in natural mineral waters, and as these substances are supposed to increase the medicinal value of the water, small quantities of them are often added to artificial mineral waters.

Compounds of Ammonium

General. As explained in Chapter XVIII, when ammonia is passed into water the two unite to form the base ammonium hydroxide, and when this base is neutralized with acids, ammonium salts are formed. Since the ammonium group is univalent, ammonium salts resemble those of the alkali metals in formulas; they also resemble the latter salts in their chemical properties, and may be conveniently described in connection with them. They all volatilize upon being heated, most of them being decomposed in the process. When heated with an aqueous solution of sodium hydroxide, they evolve ammonia (p. 201). Since the ammonia can be easily recognized, the reaction serves for the detection of the presence of ammonium compounds.

Occurrence. Small quantities of ammonium compounds are found in the soil. They are being continually absorbed by growing plants, but are returned to it again in the process of decay. They are also found in sea water and in some volcanic regions. Larger quantities are found in the Stassfurt deposits. Commercially ammonium compounds are prepared from the ammoniacal liquors produced in the manufacture of coke (pp. 306, 307).

Ammonium chloride (sal ammoniac) (NH_4Cl). This is a white solid. When heated it partly decomposes into ammonia and hydrogen chloride, which recombine, as the temperature falls:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

This salt is used in soldering, since the hydrogen chloride evolved by the heat removes the oxide from the surface of the metals. It is also used in making dry cells, in medicine, and as a chemical reagent.

Ammonium sulfate, $(NH_4)_2SO_4$. This salt resembles the chloride very closely and, being cheaper, is used in place of it when possible. It is used in large quantities as a fertilizer, the nitrogen which it contains being a very valuable food for plants.

The carbonates of ammonium. Both the normal carbonate, $(NH_4)_2CO_3$, and the acid carbonate, NH_4HCO_3, are white solids, readily soluble in water. The normal carbonate slowly decomposes into the acid carbonate, evolving ammonia:

$$(NH_4)_2CO_3 \longrightarrow NH_4HCO_3 + NH_3$$

Ammonium sulfides. When hydrogen sulfide is passed into aqua ammonia a solution containing ammonium sulfide, $(NH_4)_2S$ and ammonium acid sulfide (NH_4HS) is obtained:

$$NH_4OH + H_2S \longrightarrow NH_4HS + H_2O$$
$$2\,NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2\,H_2O$$

This solution is usually known simply as ammonium sulfide, and is used as a reagent in testing for certain metals. When exposed to the air it slowly decomposes, and the sulfur liberated in the process combines with the compounds present, forming different sulfides, such as $(NH_4)_2S_2$ and $(NH_4)_2S_3$ or, in general, $(NH_4)_2S_x$. The resulting solution is yellow and is termed *yellow ammonium sulfide* or *ammonium polysulfide.*

Flame reactions. There are several metals which, when volatilized in a colorless flame, such as that of a Bunsen burner, impart a characteristic color to the flame. Thus, sodium (or any of its compounds that will volatilize in the heat of the flame) imparts to the flame a strong yellow color. Potassium and its compounds color the flame a pale violet, and lithium colors it a deep crimson red.

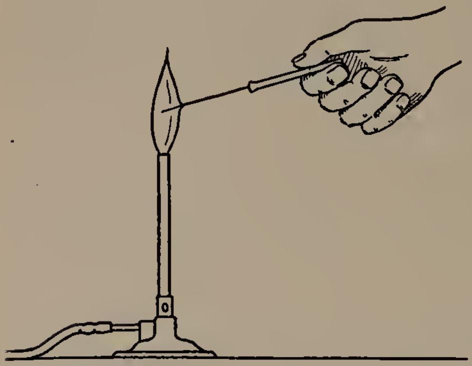


FIG. 165. Method of making a flame test

Advantage is taken of these facts in testing for the presence of the elements in different substances. The test is best made by using a platinum wire one end of which is fused into a piece of glass tubing that serves as a handle. The other end of the wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance), and the wire with the adhering particles is held in the outer edge of the base of the Bunsen flame (Fig. 165).

EXERCISES

1. What is an alkali? Can a metal itself be an alkali?

2. Write equations showing how the following changes may be brought about, giving the general principle involved in each change: $NaCl \longrightarrow Na_2SO_3$, $Na_2SO_3 \longrightarrow NaCl$, $NaCl \longrightarrow NaBr$, $Na_2SO_4 \longrightarrow NaNO_3$, $NaNO_3 \longrightarrow NaHCO_3$.

3. What carbonates are soluble?

4. State the conditions under which the reaction represented by the following equation can be made to go in either direction:

$$Na_2CO_3 + H_2O + CO_2 \rightleftarrows 2\,NaHCO_3$$

5. Account for the fact that solutions of sodium carbonate and potassium carbonate are alkaline.

6. What nonmetallic element is obtained from the deposits of Chile saltpeter?

7. Supposing concentrated hydrochloric acid (den. = 1.2) to be worth eight cents a pound, what is the value of the acid generated in the preparation of 1 ton of sodium carbonate by the Leblanc process?

8. What weight of sal soda can be prepared from 1 kg. of anhydrous sodium carbonate?

9. Write equations for the preparation of potassium hydroxide by three different methods.

10. What would take place if a bit of potassium hydroxide were left exposed to the air?

11. Write the equations for the reactions between sodium hydroxide and bromine; between potassium hydroxide and chlorine.

12. Write equations for the preparation of potassium sulfate; of potassium-acid carbonate.

13. What weight of carnallite would be necessary in the preparation of 1 ton of potassium carbonate?

14. Write the equations showing how ammonium chloride, ammonium sulfate, ammonium carbonate, and ammonium nitrate may be prepared from ammonium hydroxide.

15. Write an equation to represent the reaction involved in the preparation of ammonia from ammonium chloride.

16. What substances already studied are prepared from the following compounds: ammonium chloride; ammonium nitrate; ammonium nitrite; sodium nitrate; sodium chloride?

17. Write equations for the preparation of potassium iodide; potassium bromide.

18. How could you distinguish between potassium chloride and potassium iodide? between sodium chloride and ammonium chloride? between sodium nitrate and potassium nitrate?

19. What are the relative advantages of sodium chlorate and potassium chlorate as oxidizing agents?

20. Write the names and formulas for the different compounds that may be formed by the action of the halogen elements on the soluble bases.

CHAPTER XXXIII

SOAP; GLYCERIN; EXPLOSIVES

Introductory. At first thought one might wonder why three products so different from each other as are soap, glycerin, and explosives should be brought together for study in the same chapter. However, the grouping is a natural one industrially, for glycerin is a by-product in the manufacture of soap; and nitroglycerin, one of the most powerful explosives, is prepared from glycerin and stands in a general way as a type of an explosive compound. It is convenient, therefore, in a very brief description of these products, to include all three in the same chapter.

Composition of soap, and materials used in its preparation. Soap is a mixture of the sodium and potassium salts of oleic, palmitic, and stearic acids (p. 342). The essential materials used in the preparation of soap are as follows:

1. ***Fat or oil.*** As shown on page 342, fats and oils are largely mixtures of olein, palmitin, and stearin. The cheaper grades of these are used in making soap. Those commonly employed are a low grade of animal fat (tallow) and the cheaper vegetable oils, such as cottonseed oil, coconut oil, and palm oil.

2. ***Alkali.*** The alkali used is the hydroxide of either sodium or potassium. Sodium hydroxide is nearly always used, since it gives a hard soap, while potassium hydroxide gives a soft soap. Other bases, such as calcium hydroxide, are unavailable since they yield insoluble soaps.

Reaction taking place in the preparation of soap. When the fat and the alkali are heated together under proper conditions the olein, palmitin, and stearin present in the fat are decomposed, forming glycerin together with sodium oleate, sodium palmitate, and sodium stearate. A mixture of these three salts constitutes soap. The reactions may be illustrated by the following equation, which represents the change taking place when stearin is heated with sodium hydroxide:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{sodium hydroxide}}{3\,NaOH} \longrightarrow \underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3\,NaC_{18}H_{35}O_2}$$

In this reaction the fat is said to be *saponified*, and the process is known as *saponification.*

Commercial manufacture of soap. The oil or melted fat is poured into large iron kettles together with a solution of sodium hydroxide containing about one fourth of the amount of alkali necessary to saponify the fat. As a rule the kettles (Fig. 166) are very large, 500,000 lb. or more of soap being made in some of them in a single heating. They are provided with coils of steam pipe for heating the mixture. The fat and alkali are stirred by forcing air or live steam into the bottom of the mixture. As the heating continues, the remainder of the alkali is added. The reaction is complete in from two to five days.

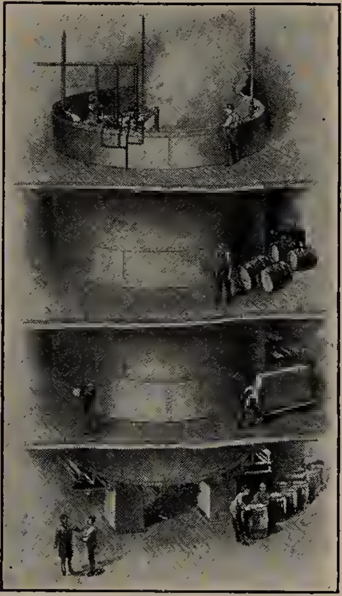


FIG. 166. A soap kettle

The soap is next removed, or *salted out,* from the mixture. This process consists in adding salt and again heating. After a time the soap rises to the top of the liquid, or *spent lye,* as it is called. The soap so obtained is purified and then run into a mixing machine (crutcher). Here it is mixed with any appropriate material which it is desired to add, such as perfume, borax, sodium silicate, or sodium carbonate. It is then run into large molds to harden, after which it is cut and pressed into cakes of the desired size. The glycerin formed in the reaction is separated from the spent lye by distillation.

Varieties of soap. *Transparent soaps* are ordinarily made by dissolving soap in alcohol. The solution is filtered and the excess of alcohol removed by distillation. *Castile soaps* are made from mixtures of olive oil with cheaper oils. The color of *mottled soaps* is produced by the addition of ferrous sulfate, Prussian blue, or some similar pigment. *Floating soaps* owe their lightness to bubbles of air. *Naphtha soaps* contain from 5 per cent to 10 per cent of petroleum naphtha. *Scouring soaps* contain from 5 per cent to 10 per cent of soap and from 80 per cent to 90 per cent of some abrasive material such as fine sand or volcanic ash. Sometimes a small percentage of sodium carbonate is also present. *Soap powders* are, as a rule, sodium carbonate or a mixture of sodium carbonate and ground soap.

Properties of soap. Soap dissolves in soft waters, giving a slightly alkaline solution due to hydrolysis. If an acid, such as hydrochloric acid, is added to the aqueous solution, the organic acids are liberated from their salts and are precipitated in the form of white insoluble solids:

$$\underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + HCl \longrightarrow NaCl + \underset{\text{stearic acid}}{H \cdot C_{18}H_{35}O_2}$$

The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water and are therefore precipitated when a calcium or magnesium compound is added to an aqueous solution of soap:

$$2\,\underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + CaCl_2 \longrightarrow 2\,NaCl + \underset{\text{calcium stearate}}{Ca(C_{18}H_{35}O_2)_2}$$

It is due to this fact that soaps do not lather with hard waters (p. 431), but form a curdy precipitate, since such waters always contain salts of calcium and magnesium in solution.

Cleansing action of soap. Attention has been called to the property possessed by soap of aiding in the formation of emulsions (p. 387). The cleansing power of soap is largely due to this property. When soap is rubbed upon the skin any oily substances present are emulsified by the soap and washed away.

Glycerin, $C_3H_5(OH)_3$. This is a colorless oily liquid having a sweet taste. It is formed whenever a fat is acted upon by an alkali and consequently is a by-product in the manufacture of soap. Nitric acid acts upon it, forming *glyceryl nitrate*, as indicated in the following equation:

$$C_3H_5(OH)_3 + 3\,HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3\,H_2O$$

In actually carrying out this reaction a mixture of nitric and sulfuric acid is always used; the sulfuric acid aids in the reaction by absorbing the water produced. It will be noted that the reaction is exactly similar to that of nitric acid upon a base, so that glyceryl nitrate is really a salt of nitric acid. Glyceryl nitrate is a slightly yellowish oil. It is a powerful explosive and is the chief constituent of the explosive known as nitroglycerin. The chief use of glycerin is in the preparation of this product.

Explosives. An explosion is caused by a very rapid chemical reaction which results in the formation of large volumes of gases from liquid and solid materials called *explosives*. The greater the volume change and the more rapidly it is produced, the more violent the explosion. The most common of the manufactured explosives are the following:

1. **Black gunpowder.** Ordinary black gunpowder is an intimate mixture of potassium nitrate, sulfur, and charcoal. When this mixture is ignited, reactions occur which result in the formation of both gaseous and solid products in the proportion of about 50 per cent each. The principal gaseous products are nitrogen and the oxides of carbon, while the solid products are chiefly potassium carbonate, potassium sulfate, and potassium sulfide. A laboratory experiment with an average powder showed that 1 g. of the powder formed on explosion 271 cc. of gas measured at 0° and 760 mm. At the temperature of explosion this volume, of course, would be greatly increased.

2. **Nitroglycerin.** As stated above, nitroglycerin is made by the action of a mixture of nitric and sulfuric acids upon glycerin and is composed chiefly of glyceryl nitrate. It is one of our most powerful explosives — much more powerful than black gunpowder. The changes that take place in its decomposition are represented in a general way in the following equation:

$$4\,C_3H_5(NO_3)_3 \longrightarrow 12\,CO_2 + 6\,N_2 + 10\,H_2O + O_2$$

One volume of nitroglycerin yields on explosion about 1300 volumes of gas, which is expanded by the heat of the reaction to over 10,000 volumes. Pure nitroglycerin is very dangerous because of the ease with which it is set off. Large quantities are used in making *dynamite*, in which form it is not exploded so readily by jarring and can be transported with less danger. Ordinary dynamite consists of a mixture of sodium nitrate, nitroglycerin, and wood pulp, the latter acting as an absorbent for the nitroglycerin.

3. **Nitrocellulose.** Just as glycerin is changed into nitroglycerin by the action of a mixture of nitric and sulfuric acids, so cellulose (p. 328) by a similar treatment yields *nitrocellulose*. Nitrocellulose is prepared from a pure form of cellulose, such as cotton, and resembles cotton in appearance. Like nitroglycerin, it is a far more powerful explosive than black gunpowder. If ignited under ordinary conditions, it will burn quietly. If subjected to a sudden shock (such as may be produced by the explosion of a small percussion primer) the nitrocellulose

decomposes with enormous violence. The products of the decomposition are all colorless gases; hence the use of this explosive in making *smokeless* gunpowder. When nitrocellulose is used for this purpose it is necessary to modify the pure material somewhat, as otherwise the violence of the explosion would shatter any firearms in which the powder was used. This is done by mixing nitrocellulose with sufficient alcohol and ether to form a plastic mass, which is then molded into the form of rods (grains) with a number of perforations through the rods. Fig. 167 shows the form of the grains used in the large guns of our navy. *Gelatin dynamite* is made by stirring nitrocellulose into nitroglycerin. It forms a jellylike mass and is a very powerful explosive.

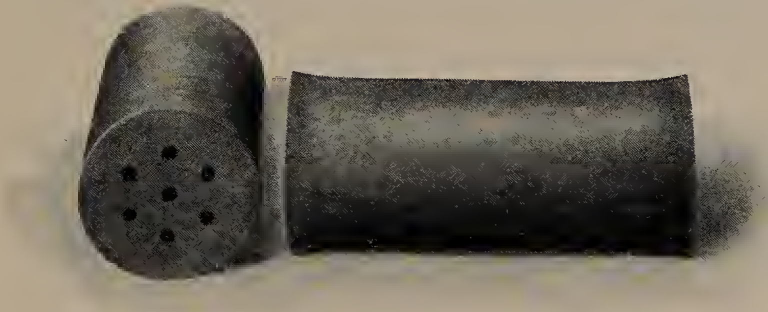


Fig. 167. Powder grains for large guns (natural size)

4. **Trinitrotoluene, $C_7H_5(NO_2)_3$; picric acid, $C_6H_2(NO_2)_3OH$.** In connection with the great war there has been developed a powerful explosive known as trinitrotoluene. It is prepared by the action of nitric acid on toluene (p. 336). It is a white solid and can be transported with safety. Picric acid is also a powerful explosive. It is a yellow solid made by treating phenol (p. 337) with nitric acid.

EXERCISES

1. In what way does aqua ammonia assist in the removal of grease?
2. For what is lye used as a household article?
3. What effect will the softening of a city water supply have on soap consumption?

4. Why will gas which burns quietly in a stove explode violently if a sufficient quantity of it is allowed to escape into a room and is then ignited?

5. What is the significance of the word *glycerin*?

6. Why not use sodium nitrate in making gunpowder?

7. Why is the ordinary black gunpowder comparatively not a very powerful explosive?

8. Why are some gunpowders smokeless and others not?

9. In some cities garbage is being utilized as a source of glycerin. Suggest the chemistry involved in the process.

10. Why not use dynamite as an explosive in guns?

11. Why does the removal of water by sulfuric acid assist in making nitroglycerin?

CHAPTER XXXIV

THE CALCIUM FAMILY; FERTILIZERS

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	CARBONATE DECOMPOSES
Calcium . . .	Ca	40.07	1.55	810°	at dull-red heat
Strontium . . .	Sr	87.63	2.54		at white heat
Barium	Ba	137.37	3.75	850°	scarcely at all

The family. The calcium family consists of the very abundant metal calcium and the rarer metals strontium and barium. These three metals are often termed the *alkaline earth* metals. Radium also occurs in this family (see the periodic arrangement of the elements), but it is more convenient to discuss it in connection with the element uranium, to which it bears a peculiar relation.

1. ***Occurrence.*** Like the alkali metals, the alkaline earth metals do not occur free in nature. Their most abundant compounds are the carbonates and sulfates, calcium also occurring in large quantities in the form of the phosphates and silicates.

2. ***Preparation.*** The metals are prepared by the electrolysis of their melted chlorides or hydroxides. Calcium is the most easily prepared.

3. ***Properties.*** The three metals resemble one another very closely. They are silvery white in color and are somewhat harder than lead. They decompose water at ordinary temperatures, forming hydroxides and liberating hydrogen, although not so readily as do the alkali metals.

When ignited in air they burn with brilliancy, forming oxides. These oxides combine with water to form hydroxides.

4. ***Compounds.*** The alkaline earth metals act as bivalent elements in the formation of salts. The corresponding salts of the three metals are similar to one another and show a regular gradation in many of their properties. Unlike the alkali metals, their carbonates, phosphates, and silicates are insoluble in water. Barium sulfate is also insoluble, while the sulfates of calcium and strontium are but sparingly soluble. When volatilized in a colorless flame (p. 414) the compounds of each of the three metals impart a characteristic color to the flame, those of calcium making the flame orange in color, those of strontium making it crimson, and those of barium making it green.

Calcium

Occurrence. Calcium is one of the abundant elements. In the form of a carbonate it occurs in a number of different forms, such as limestone and marble. The most important of its mineral compounds are the following:

Calcite	$CaCO_3$	Wollastonite	$CaSiO_3$
Phosphorite	$Ca_3(PO_4)_2$	Gypsum	$CaSO_4 \cdot 2\,H_2O$
Fluorite	CaF_2	Anhydrite	$CaSO_4$

Preparation. Calcium is prepared commercially by the electrolysis of the melted chloride in the following way:

The apparatus consists of a cylindrical iron vessel (Fig. 168), through the bottom of which extends the iron cathode *A*. The anodes (*B*, *B*), several in number, are placed about the sides of the vessel. The calcium separates in a molten condition at the cathode *A* and rises in the form of globules to the lower surface of a solid stick of calcium (*D*), suspended above the cathode. There it is chilled by a water-cooling device *C*, *C*, and adheres to the stick of calcium, which is slowly raised as it increases in length.

Properties. Calcium is a silver-white metal only a little heavier than water and melting at 810°. It combines readily with many of the elements and when ignited burns in oxygen with dazzling brilliancy. Like sodium and potassium, it decomposes water, forming a hydroxide and hydrogen. As yet it has few commercial applications.

Calcium oxide (lime) (CaO). Pure calcium oxide can be prepared by burning calcium in oxygen or by heating the nitrate or the carbonate. The more or less impure oxide, known commercially as *lime* or *quicklime*, is prepared on a large scale by heating limestone, which is chiefly calcium carbonate ($CaCO_3$). When heated the calcium carbonate decomposes according to the following equation:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

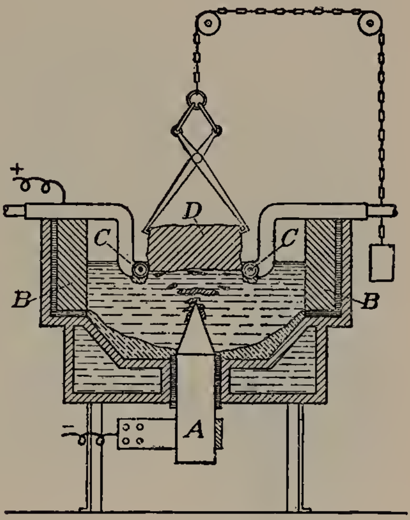


FIG. 168. The preparation of calcium by electrolysis

The reaction is reversible, so that in manufacturing practice the decomposition is effected under conditions that will conduct away the carbon dioxide as fast as it is formed.

Ordinary lime is a white amorphous substance. When heated intensely, as in the oxyhydrogen flame, it gives a brilliant light called the *limelight*. It melts only in the heat of the electric furnace. Water acts upon lime with the evolution of a great deal of heat,—whence the name *quicklime*, or *live lime*, — the process being called *slaking*. The equation is

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15,540 \text{ cal.}$$

Because of its affinity for water it is used for drying gases. It also absorbs carbon dioxide, forming the carbonate:

$$CaO + CO_2 \longrightarrow CaCO_3$$

Lime exposed to air is therefore gradually converted into the hydroxide and the carbonate and will no longer slake with water. It is then said to be *air-slaked.* Lime is produced in enormous quantities for use in making calcium hydroxide.

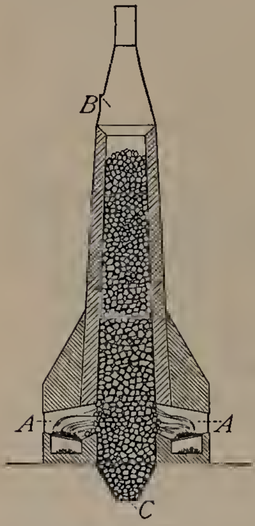


Fig. 169. The vertical section of a modern limekiln

Commercial production of lime. A vertical section of the newer form of limekiln is shown in Fig. 169. The kiln is about 50 ft. in height. A number of fire boxes, or furnaces (*A*, *A*), are built around the lower part, all leading into the central stack. The kiln is filled with limestone through a swinging door *B*. The hot products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*. This serves the purpose of cooling the hot lime at the base of the furnace, of furnishing heated oxygen for the combustion, and of removing the carbon dioxide from the kiln. The lime is dropped into cars run under the furnace. Generally a number of these kilns are operated together, as shown in Fig. 170.

Calcium hydroxide (slaked lime), $Ca(OH)_2$. This compound is prepared by adding water to lime, as explained above. When pure it is a light white powder. It is sparingly soluble in water. Moreover, its solubility diminishes with rise in temperature. The aqueous solution is called *limewater.* Owing to its cheapness calcium hydroxide is used in the industries whenever an alkali is desired. It is used in the preparation of ammonia, bleaching powder, and the hydroxides of sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from coal gas, to remove the hair from hides in making leather, for making mortar and plaster, and for liming soils (p. 437).

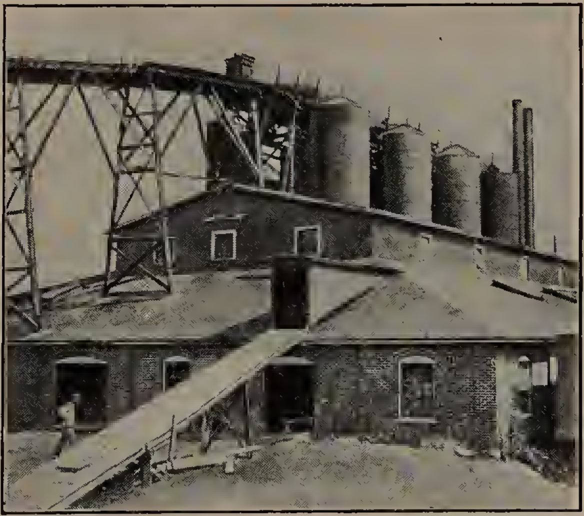


FIG. 170. A group of limekilns in a modern plant

Mortar and plaster. Mortar is a mixture of calcium hydroxide and sand. When it is exposed to the air or spread upon porous materials moisture is removed from it (partly by absorption into the porous materials and partly by evaporation) and the mortar becomes firm, or *sets.* At the same time carbon dioxide is slowly absorbed from the air, and hard calcium carbonate is formed:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous; it also prevents too much shrinkage. Plaster is a mixture of calcium hydroxide and hair, the latter serving to hold the mass together.

Bleaching powder. When chlorine is passed over calcium hydroxide there is formed a white solid compound having the formula $CaOCl_2$ and known as *bleaching powder*, *chloride of lime*, or simply *bleach*:

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

When this compound is treated with an acid, chlorine is evolved:

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

When exposed to the air, bleaching powder is slowly acted upon by moisture and carbon dioxide, with the liberation of hypochlorous acid (HClO), which is a good disinfectant.

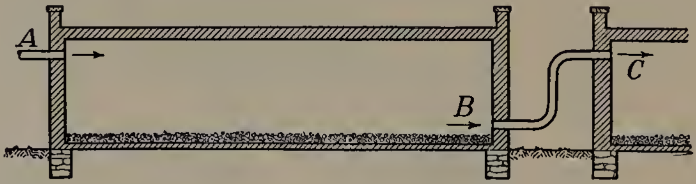


Fig. 171. Diagram of a plant for making bleaching powder

Bleaching powder is prepared in large quantities for use as a bleaching agent, as a disinfectant, and as an agent for purifying city water supplies. The commercial product generally contains from 35 to 37 per cent of available chlorine.

In the commercial preparation of bleaching powder the calcium hydroxide is spread to a depth of 2 or 3 inches upon the floor of a room, usually made of lead or concrete (Fig. 171). The chlorine, generated by the electrolysis of sodium chloride, enters near the top at *A*. Any unabsorbed chlorine passes out at *B* and into the adjoining chamber at *C*.

Calcium carbonate ($CaCO_3$). Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form and sometimes constitutes whole mountain ranges. Limestone is never pure calcium carbonate, but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. Pearls, coral, and various shells are largely calcium carbonate. *Calcite* is a very pure, crystalline form and often is found in large transparent crystals (Fig. 172) called *Iceland spar*. *Marble* is composed of very small calcite crystals.

Calcium carbonate is an example of a *dimorphous* compound; that is, it crystallizes in two different forms. Thus, calcite crystals belong to the hexagonal system (see Appendix), while aragonite, another form found in nature, forms crystals belonging to the rhombic system.

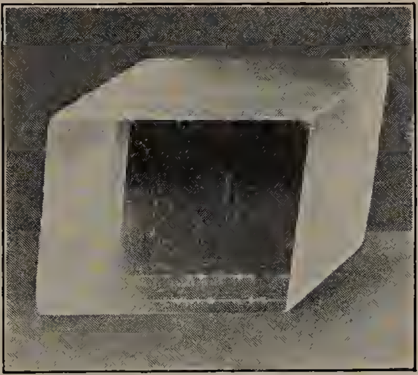


Fig. 172. A crystal of Iceland spar

In the laboratory pure calcium carbonate can be prepared by treating a soluble calcium salt with a soluble carbonate:

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2\,NaCl$$

When prepared in this way it is a soft white powder often called *precipitated chalk* and is much used as a polishing powder (tooth powder).

The natural varieties of calcium carbonate find many uses, as in the preparation of lime and of carbon dioxide; in metallurgical operations, especially in blast furnaces; in the manufacture of soda and glass; for building stone; and for ballast for roads.

Calcium acid carbonate, $Ca(HCO_3)_2$. Calcium carbonate is almost insoluble in pure water. It readily dissolves, however, in water which holds carbon dioxide in solution. This is due to the fact that the carbonate combines with the carbonic acid present in the water and forms calcium acid carbonate, which is soluble:

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2$$

The resulting acid carbonate exists only in solution, since it is unstable and decomposes into the normal carbonate on heating or on evaporation of its solution.

Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, being held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation of large caves in limestone rock, such as the Mammoth Cave in Kentucky.

Calcium sulfate ($CaSO_4$). Calcium sulfate occurs in nature in several different forms, the most common of which is *gypsum* ($CaSO_4 \cdot 2\,H_2O$). This is quarried in large amounts in New York, Michigan, and Oklahoma. It is used as a filler in making paper (p. 330), as a constituent of fertilizers, and especially in making *plaster of Paris.*

Calcium sulfate is but slightly soluble in water and is precipitated in the form of a fine white powder when concentrated solutions of a calcium salt and some sulfate are mixed together.

Plaster of Paris, $(CaSO_4)_2 \cdot H_2O$. This is a fine white powder obtained by carefully heating gypsum. When water is added to the powder a plastic mass is formed which quickly hardens, or *sets.* This property makes it valuable for molding casts, for stucco work, and for a finishing coat on plastered walls. Broken bones are often held in place by casts of plaster of Paris until they grow together.

In the manufacture of plaster of Paris the temperature must not be allowed to rise much above 125°; otherwise the anhydrous salt is formed, and this combines with water so slowly as to render it worthless for the purposes for which plaster of Paris is used.

Hard water. Waters containing compounds of calcium and magnesium in solution are called *hard* waters. The hardness of water may be of two kinds: (1) temporary hardness and (2) permanent hardness.

1. ***Temporary hardness.*** We have seen that when water charged with carbon dioxide comes in contact with limestone a certain amount of the latter dissolves, owing to the formation of the soluble acid carbonate of calcium. The hardness of such waters is said to be temporary, since it may be removed by boiling. The heat changes the acid carbonate into the insoluble normal carbonate, which then precipitates, rendering the water *soft*:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

Such waters may also be softened by the addition of sufficient lime or calcium hydroxide to convert the acid carbonate of calcium into the normal carbonate:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2\,H_2O$$

2. ***Permanent hardness.*** The hardness of water may also be due to the presence of the sulfate or the chloride of either calcium or magnesium. Boiling the water does not affect these salts; hence such waters are said to have permanent hardness. They may be softened, however, by the addition of sodium carbonate, which precipitates the calcium and magnesium as insoluble carbonates:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

This process is sometimes called "breaking" the water.

Commercial methods for softening water. The average water of a city supply contains not only the acid carbonates of calcium and magnesium but also the sulfates and chlorides of these metals, together with other salts in smaller quantities.

Such waters are softened on a commercial scale by the addition of the proper quantities of calcium hydroxide and sodium carbonate. The calcium hydroxide precipitates the acid carbonates, while the sodium carbonate precipitates the other soluble salts of calcium and magnesium. The amounts of calcium hydroxide and sodium carbonate required to soften any given water are calculated from a chemical analysis of the water. It will be noticed from the equations that the water softened in this way contains sodium sulfate and sodium chloride, but the presence of these salts is not objectionable.

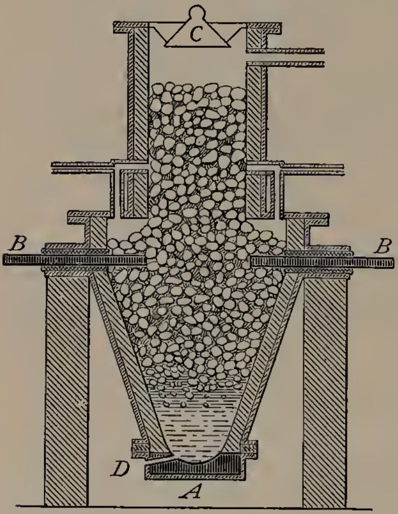


FIG. 173. A furnace for the manufacture of calcium carbide

Calcium carbide (CaC_2). This compound is prepared on a large scale for use in the manufacture of acetylene (p. 302) and in making fertilizers. It is made by heating a mixture of lime and coke in an electric furnace:

$$CaO + 3\,C \longrightarrow CaC_2 + CO$$

The pure carbide is a colorless, transparent solid. The commercial article is a dull-gray porous substance which contains many impurities. It is placed on the market in air-tight containers.

Commercial preparation. While calcium carbide was first prepared in 1836, it was not until 1893 that it became a commercial product. The general principles involved in its preparation are illustrated in Fig. 173, which represents a simple type of carbide furnace. The base of the furnace is provided with a large block of carbon (*A*), which serves as one of the electrodes. The other electrodes (*B*, *B*), several in number, are arranged horizontally at some distance above this. A mixture of coal and lime is fed into the furnace through the trap top *C*, and in the lower part of the furnace this mixture becomes intensely heated and forms liquid carbide. This is drawn off through the tap hole *D*.

Calcium cyanamide ($CaCN_2$). When nitrogen is passed over hot calcium carbide the two react, forming a compound known as calcium cyanamide:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The commercial product contains about 60 per cent of the cyanamide; the remaining 40 per cent consists chiefly of carbon and lime. This product is known as *lime-nitrogen.* This is ground and mixed with water (which slakes the lime) and in this form is sold as a fertilizer under the name *cyanamide.* Its value as a fertilizer lies in the fact that all of its nitrogen is available as a plant food.

Calcium cyanamide promises also to become of importance in the commercial preparation of ammonia and sodium cyanide, both of which can readily be obtained from it in a manner indicated by the following equations:

$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3$$
$$CaCN_2 + C + 2\,NaCl \longrightarrow CaCl_2 + 2\,NaCN$$

The nitrogen used in the manufacture of cyanamide is obtained from liquid air as explained on page 131. By means of the reactions expressed in the above equations it is possible, therefore, to convert the nitrogen of the air into important compounds of nitrogen.

Phosphates of calcium. With phosphoric acid, calcium forms three salts, the names and formulas of which are as follows:

Normal calcium phosphate	$Ca_3(PO_4)_2$
Calcium monohydrogen phosphate	$CaHPO_4$
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_2$

The normal phosphate, usually called simply calcium phosphate, is found in quantities in nature, largely in the form of rock phosphate or *phosphorite* and as a constituent of *apatite.* It is the chief mineral constituent of bones, the ash of which contains about 80 per cent of this compound. The phosphates are of great importance in connection with the subject of fertilizers (see p. 353 and end of this chapter).

Other compounds of calcium. ***Calcium chloride*** ($CaCl_2$) occurs in sea water and is formed in large quantities as a by-product in the Solvay process for making sodium carbonate. The anhydrous salt readily absorbs moisture and is used as an agent for drying gases. A solution of the salt is used as a brine in the manufacture of ice (p. 111). It has also been used to lay the dust on roads, and mines have been sprinkled with it in the hope of preventing dust explosions. ***Calcium fluoride*** (CaF_2) occurs in nature in the form of *fluorite.* It is mined in large quantities, especially in Illinois, and is used in the preparation of hydrofluoric acid, in the manufacture of opaque glass, and in various metallurgical operations. ***Calcium sulfide*** (CaS) is a by-product in the Leblanc process for making sodium carbonate. The commercial salt is sometimes used as a luminous paint, since, after exposure to a bright light, it will glow in the dark. ***Calcium acid sulfite,*** $Ca(HSO_3)_2$, is used as a preservative, and in large quantities in the manufacture of paper (p. 330). A number of ***calcium silicates*** are known and derive their chief interest from the fact that they are important constituents of cement and glass.

STRONTIUM AND BARIUM

General. These elements themselves are much rarer than calcium, are difficult to prepare, and have no commercial uses. Their most abundant minerals are the following:

Celestite	$SrSO_4$	Barite	$BaSO_4$
Strontianite	$SrCO_3$	Witherite	$BaCO_3$

The compounds of strontium and of barium are similar in composition and properties to the corresponding compounds of calcium. The following are of importance:

Oxides of barium. Barium oxide (BaO) can be obtained by strongly heating the nitrate:

$$2\,Ba(NO_3)_2 \longrightarrow 2\,BaO + 4\,NO_2 + O_2$$

When heated to a low red heat in the air the oxide combines with oxygen, forming the peroxide, BaO_2, which is used in making hydrogen peroxide (p. 81).

Barium chloride ($BaCl_2$). Barium chloride is a white solid, and from its solution it crystallizes as the hydrate $BaCl_2 \cdot 2\,H_2O$. It is used in the laboratory as a reagent to detect the presence of sulfuric acid or soluble sulfates, since it reacts with these to form the insoluble barium sulfate.

Barium sulfate (barite) ($BaSO_4$). Barium sulfate occurs in nature as a heavy white mineral known as *barite.* It is precipitated as a crystalline powder when a barium salt is added to a solution of a sulfate or to sulfuric acid:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

It is used in large quantities in the manufacture of paint.

Barium nitrate, $Ba(NO_3)_2$. This compound is an oxidizing agent. When ignited with some oxidizable substance it gives a brilliant green light and is used for this purpose in the manufacture of fireworks.

Strontium hydroxide, $Sr(OH)_2$. The method of preparation of strontium hydroxide is analogous to that of calcium hydroxide. It crystallizes from hot water in the form of the hydrate $Sr(OH)_2 \cdot 8\,H_2O$. Strontium hydroxide has the property of forming with sugar an insoluble compound which can easily be separated again into its constituents. It has therefore been used in the sugar refineries to extract sugar from impure mother liquors from which the sugar will not crystallize.

Strontium nitrate, $Sr(NO_3)_2$. This compound imparts a crimson color to flames and is used in the manufacture of fireworks to produce a red light.

FERTILIZERS

Plant food; fertilizers. With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant derives its nourishment from the soil. In order that vegetation may thrive it is essential, therefore, that the soil should contain an adequate supply of appropriate plant food. Moreover, since this supply is continually being drawn upon by the growing plant, it is necessary, in order that the soil may retain its fertility, that the ingredients so withdrawn shall be returned to it. It is for this purpose that fertilizers are used.

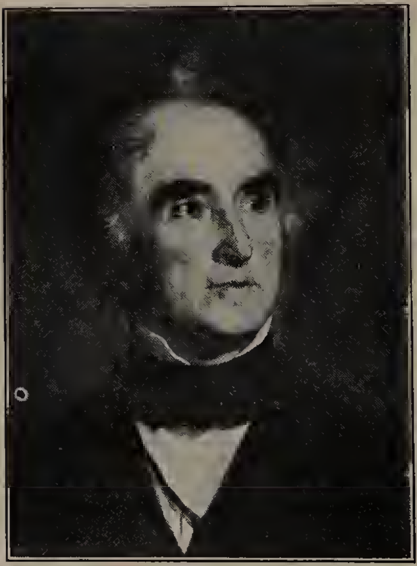


FIG. 174. Justus Liebig (1803–1873)

A great German chemist and teacher. A pioneer, especially in agricultural chemistry and soil fertility

Constituents of fertilizers. While a number of elements are essential to the growth of the plant, experience has shown that in general the fertility of the soil may be maintained by adding three substances: (1) nitrogenous matter, (2) phosphates of calcium, and (3) compounds of potassium. Compounds of sulfur are also essential, but they are usually present in sufficient quantities.

Sources of fertilizers. The commercial sources of each of the constituents of fertilizers are as follows:

1. ***Nitrogenous matter.*** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, and cyanamide; also nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and, especially, animal excrements.

2. ***Phosphates.*** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source, however, is entirely inadequate, and the great supply comes from the rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are quarried in large quantities, especially in Florida (Fig. 142) and Tennessee. Since calcium phosphate is nearly insoluble, the rock is ground and then treated with sulfuric acid. This converts the insoluble calcium phosphate into the soluble calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow 2\,CaSO_4 + Ca(H_2PO_4)_2$$

The resulting mixture of calcium sulfate and calcium acid sulfate is a powder known as *superphosphate of lime* and is a valuable fertilizer. The calcium sulfate present in the mixture adds to the value of the fertilizer, furnishing sulfur and improving the physical qualities of the soil. Certain products (slags) formed in the manufacture of steel contain phosphorus and are used in fertilizers.

3. ***Potassium compounds.*** These are obtained chiefly from the Stassfurt mines. Kainite ($KCl \cdot MgSO_4 \cdot 3\,H_2O$) is the most common of the minerals used (p. 408). Wood ashes are excellent, but the supply is limited.

Commercial fertilizers are, as a rule, mixtures of the three fundamental materials mentioned above. The composition of the fertilizer is varied according to the crop to be grown and also according to the nature of the soil upon which the fertilizer is to be used

Liming soils. Sometimes a soil becomes sour, or acid, owing to the formation of acids which are often derived from decomposing vegetable matter. Certain plants, such as mosses and huckleberries, will thrive in acid soil, but grass, clover, and grain crops will not. In such cases the soil must be *sweetened* by spreading calcium hydroxide (slaked lime) upon it to neutralize the acids present, the process being called *liming* the soil. An acid soil may be detected by moistening strips of blue litmus and covering them for a few minutes with the moist soil.

EXERCISES

1. What properties have the alkaline earth metals in common with the alkali metals? In what respect do they differ?

2. Write the equation for the reaction between calcium carbide and water.

3. How is calcium chloride removed from hard water?

4. Would air-slaked lime do for making mortar? Would it serve for liming acid soils?

5. Why would you expect calcium carbide to contain impurities?

6. How do you explain the fact that calcium carbonate can be decomposed into calcium oxide and carbon dioxide, and yet calcium oxide absorbs carbon dioxide from the air to form the carbonate?

7. Could barium hydroxide be used in place of calcium hydroxide in testing for carbon dioxide?

8. Calcite and gypsum often resemble each other in appearance. How could you easily distinguish between the two?

9. Suggest a method for preparing nitric acid from calcium cyanamide.

10. Calcium acid sulfite is prepared from calcium hydroxide in a manner perfectly analogous to the preparation of the acid carbonate. Write the equation for the reactions involved.

11. How could you prepare calcium chloride from calcium sulfate? barium chloride from barite?

12. How could you prove that dried mortar contains calcium carbonate and sand?

13. Mention different advantages gained by a city from softening its water supply.

14. What weight of plaster of Paris can be made by heating 1 ton of gypsum?

15. What weight of limestone is necessary to prepare 10 tons of lime?

16. What weight of water is necessary to slake 1 ton of lime?

17. Calculate the weight of calcium oxide present in the lime made by heating 1 ton of limestone containing 90 per cent of calcium carbonate. What weight of water would be required to slake the resulting calcium oxide?

18. The heat evolved in the slaking of 100 kg. of lime would raise the temperature of what weight of water from room temperature (say 18°) to boiling?

19. A certain city uses 10,000,000 gal. of water daily, and 100 gal. of the water contains 120 g. of calcium acid carbonate and 30 g. of calcium sulfate. What weights of calcium hydroxide and sodium carbonate are required to soften the daily water supply?

20. In the manufacture of fertilizer what weight of sulfuric acid containing 50 per cent by weight of hydrogen sulfate would be necessary for the treatment of 1 ton of phosphate rock, on the supposition that the only reaction taking place is expressed by the following equation:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow 2\,CaSO_4 + Ca(H_2PO_4)_2$$

21. Starting with limestone and sulfur, how could you prepare the calcium acid sulfite used in the manufacture of paper?

CHAPTER XXXV

THE MAGNESIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	OXIDE
Magnesium . .	Mg	24.32	1.74	651°	920°	MgO
Zinc	Zn	65.37	7.10	419.4°	950°	ZnO
Cadmium . .	Cd	112.40	8.64	320.9°	778°	CdO

The family. In the magnesium family are included the four elements magnesium, zinc, cadmium, and mercury. Between the first three of these metals there is a close family resemblance, such as has been traced between the members of the two preceding families. In some respects mercury is more closely related to copper and will be studied in connection with that metal.

Properties. At ordinary temperatures oxygen has but little action upon the members of this family. At high temperatures, however, combination takes place rapidly, with the formation of oxides. Magnesium rapidly decomposes boiling water, while zinc and cadmium have but slight action upon it. All three dissolve in acids, with the liberation of hydrogen.

Compounds. The members of the family are bivalent in their compounds, so that the formulas of their salts resemble those of the alkaline earth metals. Like the latter metals, their normal carbonates, normal phosphates, and normal silicates are insoluble in water. Their sulfates, however, are readily soluble. Unlike both the alkali metals and the alkaline earth metals, the hydroxides of the metals of the magnesium family are nearly insoluble in water and are much more readily decomposed by heat, forming water and the oxide of the metal.

MAGNESIUM

Occurrence. Magnesium is a very abundant element in nature, ranking a little below calcium in this respect. Like calcium, it is a constituent of many rocks and also occurs in the form of soluble salts. Dolomite ($CaCO_3 \cdot MgCO_3$) and magnesite ($MgCO_3$) occur in large quantities. Asbestos, talc, and serpentine are silicates of magnesium. The element is also a constituent of *chlorophyll*, the green coloring matter of plants.

Preparation. The metal magnesium, like most metals whose oxides are difficult to reduce with carbon, is made by electrolysis, the anhydrous chloride or the mineral carnallite (p. 408) being used as the electrolyte. The electrolyte is melted in an iron pot, which also serves as the cathode in the electrolysis, while a rod of carbon dipping into the melted salt serves as the anode. The apparatus is very similar to those employed in the preparation of sodium and calcium.

Properties. Magnesium is a light, silver-white metal just heavy enough to sink in water. It is usually sold in the form of thin ribbon or of wire or as a powder. Air does not act rapidly upon it, but a thin film of basic carbonate forms upon its surface, dimming its bright luster. It combines directly with most of the nonmetals, even with nitrogen. The common acids dissolve it, with the formation of the corresponding salts. It can be ignited readily, and in burning it gives a brilliant white light. This light is very rich in the rays which affect photographic plates, and the metal, in the form of fine powder, is extensively used in the production of *flash lights* for flash-light photography, for white lights in pyrotechnic displays, and for rockets to light battlefields by night. When used for this purpose the powder is mixed with an oxidizing agent, potassium chlorate being the one commonly employed.

Magnesium oxide (magnesia) (MgO). Magnesium oxide, sometimes called *magnesia* or *magnesia usta*, resembles lime in many respects. It is much more easily formed than lime and can be made in the same way; namely, by heating the carbonate. It is a white powder, very soft and bulky, and is unchanged by heat even at very high temperatures. For this reason it is used in the manufacture of crucibles, for lining furnaces, and for other purposes where a refractory basic substance is needed.

Magnesium hydroxide, $Mg(OH)_2$. The hydroxide of magnesium is but slightly soluble in water and can be precipitated by adding a soluble base to a salt of magnesium:

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

It dissolves sufficiently to give a slightly alkaline reaction and is a moderately strong base. It is a white amorphous substance and is converted into the oxide when heated.

Magnesium carbonate ($MgCO_3$). Magnesium carbonate occurs in a number of localities as *magnesite*, which is usually amorphous, but sometimes forms pure crystals resembling calcite. More frequently it is found associated with calcium carbonate. The mineral *dolomite* has the composition $CaCO_3 \cdot MgCO_3$. Limestone containing smaller amounts of magnesium carbonate is known as *dolomitic limestone.* Dolomite is one of the most common rocks, forming whole mountain masses. It is harder and less readily attacked by acids than limestone. It is valuable as a building stone and for foundations and as ballast for roadbeds. Like calcium carbonate, magnesium carbonate is insoluble in water, but readily dissolves in water containing carbon dioxide, forming the acid carbonate:

$$MgCO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2$$

When a solution of a magnesium salt is precipitated with sodium carbonate, there is obtained a white basic carbonate, known as *magnesia alba*, which is used as a cosmetic and as a medicine.

FIG. 175. Cross section of a boiler tube showing the deposit of scale

Boiler scale. When water which contains certain salts in solution is evaporated in steam boilers, a hard insoluble material called *scale* deposits in the boiler. The formation of this scale may be due to several distinct causes:

1. *To the deposit of calcium sulfate.* This salt, while sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently it is precipitated when water containing it is heated in a boiler.

2. *To decomposition of acid carbonates.* As we have seen, calcium acid carbonate and magnesium acid carbonate are decomposed on heating, forming insoluble normal carbonates:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

3. *To hydrolysis of magnesium salts.* Magnesium chloride and, to some extent, magnesium sulfate undergo hydrolysis when superheated in solution, and the magnesium hydroxide, being sparingly soluble, is precipitated:

$$MgCl_2 + 2\,H_2O \longrightarrow Mg(OH)_2 + 2\,HCl$$

The scale adheres tightly to the boiler tubes in compact layers (Fig. 175) and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and its resistance to reagents. Thick scale sometimes cracks, and the water coming in contact with the overheated iron causes an explosion.

Magnesium sulfate ($MgSO_4$). Like the chloride, magnesium sulfate is found rather abundantly in springs and in salt deposits. Deposits of the almost pure solid salt having the composition $MgSO_4 \cdot 7\,H_2O$ have been found in Wyoming and Washington. It is often called *Epsom salt* because of its occurrence in the waters of the Epsom springs in England.

Magnesium sulfate is used to a small extent in the preparation of sodium and potassium sulfates, for weighting cotton cloth in the dye industry, in tanning, and in the manufacture of paints and laundry soaps. To some extent it is used in medicine.

Magnesium silicates. Many silicates containing magnesium are known, and some of them are important substances. *Serpentine*, *asbestos*, *talc* (or *soapstone*), and *meerschaum* are examples of such substances. Asbestos is soft and fibrous and a nonconductor of heat and of electricity. It is used for fireproof material in a great variety of forms, such as cloth, paper, board, and rope. It is also used as a covering for pipes, furnaces, and boilers, to diminish heat radiation. It also has many uses as an insulator in electrical devices. The chief source of asbestos is the province of Quebec, Canada. Soapstone is valuable for sinks and table tops and, in finely ground form, as a toilet powder and foot ease. It is sometimes called *French chalk.* Meerschaum is used for pipe bowls and similar articles.

ZINC

Occurrence. Zinc never occurs free in nature. It is not a constituent of common rocks and minerals, and its occurrence is rather local and is confined to definite deposits or to pockets. It occurs chiefly in the following ores: sphalerite (zinc blende) (ZnS); zincite (ZnO); smithsonite ($ZnCO_3$); franklinite ($ZnO \cdot Fe_2O_3$); willemite (Zn_2SiO_4). One fourth of the world's output of zinc comes from the United States — Missouri, Kansas, and New Jersey being the largest producers.

Metallurgy. The ores employed in the preparation of zinc are chiefly the sulfide, the oxide, and the carbonate. The sulfide and the carbonate are first roasted in the air, by which process they are changed into the oxide:

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

The oxide is then mixed with coal dust, and the mixture is heated in earthenware retorts. The oxide is reduced by this means to the metallic state, and the zinc, being heated above its boiling point, distills and is collected in suitable receivers and drawn off into molds. In this form it is called *spelter.* Commercial zinc often contains impurities, especially carbon, arsenic, or iron.

Properties. Pure zinc is a rather heavy bluish-white metal with a high luster. It melts at about 420°, and if heated much above this temperature in the air, it takes fire and burns with a bluish flame. It boils at about 950°.

Many of the properties of zinc are much influenced by the temperature and previous treatment of the metal. When cast into ingots from the liquid state it becomes at ordinary temperatures hard, brittle, and highly crystalline. At 100°–150° it is malleable and can be rolled into thin sheets; at higher temperatures it again becomes very brittle. When once rolled into sheets it retains its softness and malleability at ordinary temperatures. When melted and poured into water it forms thin, brittle flakes, and in this condition is called *granulated zinc* or *mossy zinc.*

Zinc is tarnished superficially by moist air, but beyond this is not affected by it. When the metal is quite pure, sulfuric acid and hydrochloric acid act upon it very slowly; when, however, it contains small amounts of other metals, such as magnesium or copper, or when it is merely in contact with another metal brisk action takes place and hydrogen is evolved. For this reason, when pure zinc is used in the preparation of hydrogen a few drops of copper sulfate are often added to the solution to assist the chemical action. Strong alkalies dissolve zinc, liberating hydrogen.

Uses of zinc. The chief use of zinc is in the manufacture of galvanized iron. This is sheet iron or wire covered with a thin layer of zinc, which protects the iron from rusting (p. 512). About two thirds of all the zinc produced is used in this way. Sheet zinc is used as a lining for sinks and water-containers. Large quantities of the metal are used in making brass and other alloys (p. 497), in the construction of electrical batteries, and in separating silver from lead (p. 516). In the laboratory it is used in the preparation of hydrogen and, in the form of zinc dust, as a reducing agent.

Manufacture of galvanized iron. Fig. 176 shows the method used in making galvanized iron. The plates of iron pass under the rollers at *A* and on into the pot of melted zinc *B*. The zinc adheres to the iron, and the resulting plate is passed under the roller *C* to remove the excess of zinc and to render the surface smooth. Sometimes the zinc is deposited on the iron by electrolytic methods.

Zinc oxide (zinc white) (ZnO). Zinc oxide occurs in impure form in nature, being colored red by compounds of manganese or of iron. It can be prepared in the same way as magnesium oxide, namely, by heating zinc carbonate or hydroxide, but it is more often made by burning the metal.

FIG. 176. The manufacture of galvanized sheet iron

Zinc oxide is a pure-white powder which is much used as a white pigment in paints, under the name of *zinc white.* It has an advantage over white lead in that it is not changed in color by sulfur compounds, while lead compounds turn black. Many thousand tons of zinc oxide are used in paints each year. It is also used as a filler in the manufacture of rubber goods. Large quantities are used annually in the manufacture of automobile tires.

Zinc sulfate ($ZnSO_4$). This salt is readily crystallized from concentrated solutions in transparent colorless crystals which have the formula $ZnSO_4 \cdot 7\,H_2O$ and are called *white vitriol.* It is prepared commercially by the careful roasting of the sulfide:

$$ZnS + 2\,O_2 \longrightarrow ZnSO_4$$

Zinc chloride ($ZnCl_2$). This salt is very soluble in water and has a strongly acid reaction. It has germicidal properties and is used to preserve railroad ties and other timbers especially subject to decay.

Zinc sulfide (ZnS). This substance occurs as the mineral *sphalerite,* and is one of the most valued ores of zinc. Very large deposits occur in southwestern Missouri. The natural mineral is found in large crystals or masses resembling resin in color and luster. It is insoluble in water and when prepared by precipitation is white. *Lithopone* is a mixture of the two solids barium sulfate and zinc sulfide and is made by bringing together barium sulfide and zinc sulfate in solution:

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS$$

It is a valuable white pigment.

Preservation of wood. With the rapid disappearance of the forests the preservation of wood from decay (fungous growths) becomes a very important problem. When the wood is to be exposed merely to atmospheric conditions it is preserved by paints and varnishes. When it must be partly buried in the ground (railway ties, fence posts) it is treated with germicidal preservatives. Those most frequently used are zinc chloride, copper sulfate, and coal-tar creosote.

The wood is placed in closed boilers in baths of the appropriate liquid, and the air is exhausted so that the liquid may be more readily driven into the pores of the wood. Frequently the latter process is assisted by the application of considerable pressure to the liquid after the air has been pumped out.

CADMIUM

The element. This element occurs in small quantities in some zinc ores. In the course of the metallurgy of zinc the cadmium compounds undergo chemical changes quite similar to those of the zinc compounds, and the cadmium distills along with the zinc. Being more volatile, it comes over with the first of the zinc and is prepared from the first portions of the distillate by special methods of purification. The element very closely resembles zinc in most respects. Some of its alloys are characterized by having low melting points. The United States and Germany produce, in about equal quantities, the world's supply of cadmium.

Compounds of cadmium. Among the compounds of cadmium may be mentioned the chloride, $CdCl_2 \cdot 2\,H_2O$, the sulfate, $3\,CdSO_4 \cdot 8\,H_2O$, and the nitrate, $Cd(NO_3)_2 \cdot 4\,H_2O$. These are white solids soluble in water. The sulfide, CdS, is a bright-yellow substance which is insoluble in water and in dilute acids. It is valuable as a pigment in fine paints.

EXERCISES

1. What properties have the metals of the magnesium family in common with the alkali metals? with the alkaline earth metals?

2. Compare the action of the metals of the magnesium group on water with that of the other metals studied.

3. What metals already studied are prepared by electrolysis?

4. Write the equation representing the reaction between magnesium and hydrochloric acid; between magnesium and dilute sulfuric acid.

5. What is the composition of commercial lime prepared from dolomite?

6. With phosphoric acid magnesium forms salts similar to those of calcium. Write the names and formulas of the magnesium salts which one might expect to be thus formed.

7. How could you distinguish between magnesium chloride and magnesium sulfate? between Glauber's salt and Epsom salt?

8. Account for the fact that paints made of zinc oxide are not colored by hydrogen sulfide.

9. Write equations showing how the following compounds of zinc may be obtained from metallic zinc: the oxide, chloride, nitrate, carbonate, sulfate, sulfide, hydroxide.

10. How could you prepare the pigment cadmium sulfide, starting with cadmium?

11. Note the position of the alkali metals, the calcium family, and the magnesium family in the electrochemical series. How would you expect acids to act upon these metals?

12. Suggest a reason why none of the metals so far studied are found free in nature.

13. What reaction should you expect to take place if a piece of zinc is immersed in a solution of copper sulfate? Explain.

14. What weight of carnallite is necessary in the preparation of 500 g. of magnesium?

15. What weight of franklinite is necessary for the preparation of 1 ton of zinc white?

16. 1 g. of a zinc ore was dissolved in acid and the zinc present precipitated by hydrogen sulfide. The resulting zinc sulfide weighed 0.38 g. Calculate the percentage of zinc in the ore.

17. Which would yield the more zinc, 1 ton of sphalerite or 1 ton of franklinite?

CHAPTER XXXVI

THE ALUMINIUM GROUP

The group. With the exception of aluminium none of the elements of Group III of the periodic table are well known or abundant. Boron has already been considered, and the others fall naturally into two families. The one includes aluminium, together with gallium, indium, and thallium; the other, scandium and yttrium, together with a large group of elements whose oxides are collectively called the *rare earths.*

All of the elements of this group are trivalent in their compounds, though some of the rarer elements, particularly thallium, have lower valences as well. With few exceptions their salts are colorless, save when they are derived from a colored acid. The bases which these elements form are nearly all weak, and many of their salts are hydrolyzed in solution. A discussion of the rare elements of the group does not fall within the scope of an elementary text. Aluminium, however, is a very important metal, so that it will be considered somewhat in detail.

ALUMINIUM

Occurrence. Next to oxygen and silicon, aluminium is the most abundant of all the elements. The free element is not found in nature, but its compounds are widely distributed. The feldspars, which are the most abundant of all the minerals in the earth's crust, are all silicates of aluminium and either sodium, potassium, or calcium.

Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminium, chiefly in the form of clay. Some of the other forms in which aluminium occurs in nature are the following: corundum (Al_2O_3); emery (Al_2O_3 colored black with oxide of iron); cryolite (Na_3AlF_6); bauxite, a mixture of hydrated aluminium oxides ($Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3\,H_2O$) together with similar compounds of iron. Bauxite is the ore from which aluminium is prepared. In the United States the entire commercial supply now comes from Arkansas.

FIG. 177. Charles Martin Hall
1863-1914

The American chemist who developed the electrolytic method for the production of aluminium

Preparation. Aluminium was first prepared by Wöhler, in 1827, by heating anhydrous aluminium chloride with potassium:

$$AlCl_3 + 3\,K \longrightarrow 3\,KCl + Al$$

Although the metal is very abundant in nature and possesses many desirable properties, the cost of separating it from its ores was so great that it remained almost a curiosity until comparatively recent years. With the development of cheap ways of obtaining electrical energy the problem has been solved, and the metal is now produced in large quantities by the electrolysis of aluminium oxide (Al_2O_3) dissolved in melted cryolite — a method developed by the American chemist Hall (Fig. 177) in 1886.

Metallurgy. An iron box *A* (Fig. 178) about 8 ft. long and 6 ft. wide is connected with a powerful electrical generator in such a way as to serve as the cathode upon which the aluminium is deposited. Three or four rows of carbon rods *B*, *B*, dip into the box and serve as the anodes. The box is partly filled with cryolite, and the current is turned on, generating enough heat to melt the cryolite. Aluminium oxide is then added, and acts as an electrolyte, being decomposed into aluminium and oxygen. The temperature is maintained above the melting point of aluminium, and the liquid metal, being heavier than cryolite, collects on the bottom of the vessel, from which it is tapped off from time to time through the tap hole *C*.

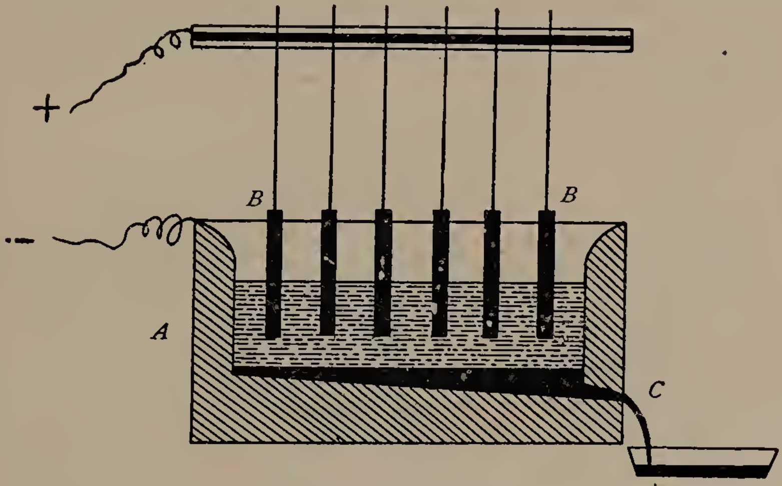


Fig. 178. Diagram illustrating the manufacture of aluminium

Properties. Aluminium is a tin-white metal which melts at 658.7° and is very light, its density being about one third that of iron. It is stiff and strong, and with frequent heating can be rolled into thin foil. It is a good conductor of heat and electricity, though not so good as copper *for a given cross section of wire.*

Aluminium is not perceptibly acted on by boiling water, and moist air merely dims its luster. Further action is prevented in each case by the formation of an extremely thin film of oxide upon the surface of the metal. It is a good reducing agent, combining with oxygen at high temperatures with the liberation of much heat:

$$4\,Al + 3\,O_2 \longrightarrow 2\,Al_2O_3 + 760{,}400 \text{ cal.}$$

Hydrochloric acid acts upon it, forming aluminium chloride; nitric acid and dilute sulfuric acid have almost no action on it; but hot concentrated sulfuric acid acts upon it, forming aluminium sulfate. Alkalies readily attack it, liberating hydrogen:

$$2\,Al + 6\,KOH \longrightarrow 2\,Al(OK)_3 + 3\,H_2$$

Salt solutions, such as sea water, corrode the metal rapidly.

Uses of aluminium. These properties suggest many uses for the metal. Its lightness, strength, and inactivity toward air and water make it well adapted for many construction and manufacturing purposes. These same properties have led to its extensive use in the manufacture of cooking utensils. Owing to its small resistance to electrical currents, it is replacing copper to some extent in electrical construction, especially for trolley and power wires. In the form of a powder suspended in a suitable liquid it makes a silvery paint used to cover iron pipes and lantern curtains. The greatest use of aluminium is in the steel industry (p. 482). *Aluminium bronze*, consisting of about 90 per cent copper and 10 per cent aluminium, has a pure-golden color, is strong and malleable, is easily cast, and is permanent in the air. *Magnalium* is an alloy of aluminium and magnesium. It is light and rigid and is used for balance beams.

Goldschmidt reduction process. Aluminium is frequently employed as a powerful reducing agent, many metallic oxides which resist reduction by carbon being readily reduced by it. The aluminium, in the form of a fine powder, is mixed with the metallic oxide, together with some substance such as fluorite to act as a flux. The mixture is ignited, and the aluminium unites with the oxygen of the metallic oxide, liberating the metal.

Thermite welding process. The property possessed by aluminium of reducing oxides with the liberation of a large amount of heat is turned into practical account in the welding of metals. The German chemist Goldschmidt was the first to use aluminium for this purpose. The welding of metals by this method may be illustrated by a single example, namely the welding of car rails — a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 179) is then clamped about the ends of the rail, leaving sufficient space so that the metal can flow in. The ends of the rails are heated to redness by the flame from a gasoline compressed-air torch directed into the opening in the mold. Just over the opening is placed the conical-shaped crucible *B*, which contains a mixture of iron, metallic oxides, and aluminium. When the ends of the rails have been heated to redness by the torch, the mixture in the crucible is ignited, and after a few seconds the crucible is opened at the bottom, and the molten metal resulting from the reaction in the crucible is allowed to flow into the mold. The molten metal surrounds the ends of the rails and, as it cools, welds them firmly together. A mixture of the metallic oxides and aluminium ready for use in welding is sold under the name of *thermite*.

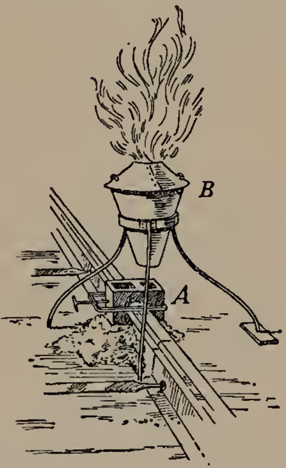


Fig. 179. Welding a rail with thermite

Aluminium oxide (Al_2O_3). This substance occurs in several forms in nature. The relatively pure crystals are called *corundum*; *emery* is a variety colored dark gray or black, usually by iron compounds. In transparent crystals, tinted different colors by traces of impurities, it forms such precious stones as the *sapphire*, *ruby*, *topaz*, and *oriental amethyst.* All these varieties are very hard, falling little short of the diamond in this respect. The cheaper forms, corundum and emery, are used for cutting and grinding purposes. Chemically pure aluminium oxide can be made by igniting the hydroxide, when it forms a white powder:

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O$$

The artificially prepared oxide is largely used in the preparation of aluminium. Some laboratory utensils, such as crucibles and tubes, are made of aluminium oxide, which is given the trade name *alundum.* The same material is used for cutting and polishing metals.

Artificial gems. A number of gems are now prepared in the laboratory from molten aluminium oxide. The white sapphires so extensively advertised are simply the pure oxide. By incorporating with the melted oxide small percentages of certain metallic oxides, different tints or colors are obtained, and in this way are prepared such gems as the ruby, the oriental amethyst, and the yellow sapphires and blue sapphires, all of which are practically identical in composition and properties with the natural stones.

Aluminium hydroxide, $Al(OH)_3$. The hydroxide can be prepared by adding ammonium hydroxide to any soluble aluminium salt, forming a colloidal precipitate which is insoluble in water but very hard to filter. When heated it is decomposed, forming the oxide and water. It dissolves in most acids to form soluble salts, and in the strong bases to form aluminates, as indicated in the equations

$$Al(OH)_3 + 3\,HCl \longrightarrow AlCl_3 + 3\,H_2O$$
$$Al(OH)_3 + 3\,NaOH \longrightarrow Al(ONa)_3 + 3\,H_2O$$

It may act, therefore, either as a weak base or as a weak acid, its action depending upon the character of the substances with which it is in contact. It is therefore an amphoteric hydroxide (p. 361).

When heated gently the hydroxide loses part of its hydrogen and oxygen according to the equation

$$Al(OH)_3 \longrightarrow AlO \cdot OH + H_2O$$

This substance, the formula of which is frequently written $HAlO_2$, is a more pronounced acid than is the hydroxide, and its salts are frequently formed when aluminium compounds are fused with alkalies. The magnesium salt $Mg(AlO_2)_2$ is called spinel, and many other of its salts, called aluminates, are found in nature.

Use of aluminium hydroxide in water purification. The value of aluminium hydroxide in the purification of water (p. 71) is due largely to its colloidal character. This colloid is dispersed all through the water, and as it slowly coagulates and settles it carries with it any suspended matter present, including microörganisms and coloring materials. The colloidal hydroxide is formed (as hydrogel) by dissolving in the water some cheap salt which readily hydrolyzes, such as aluminium sulfate:

$$Al_2(SO_4)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2SO_4$$

As a rule there is sufficient basic material present in the water to combine with the sulfuric acid set free, so that no acid is left in the water as a result of this treatment; otherwise some basic substance (such as calcium hydroxide) must be added with the aluminium sulfate.

Fig. 180 illustrates the use of aluminium sulfate in purifying water. The cylinder *A* contains impure water. *B* is a similar cylinder of water to which some aluminium sulfate has been added. The aluminium hydroxide formed by hydrolysis is slowly settling in the water, carrying with it the impurities. The appearance of the water after the aluminium hydroxide has settled is shown in *C*.

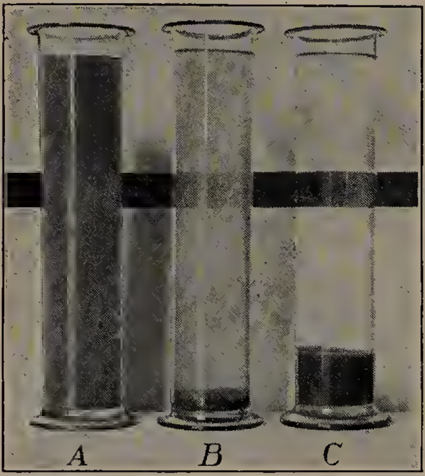


FIG. 180. Purification of water by aluminium sulfate

Use of aluminium hydroxide in dyeing. Aluminium hydroxide either combines with or absorbs many soluble coloring substances, forming insoluble products. This property leads to its wide use in the dyeing industry. Most of the dyes are prepared from compounds obtained from coal tar (hence the term *coal-tar dyes*). Many of these will not adhere to natural fibers, such as cotton; that is, they will not dye fast. It is often possible to dye such cloth in the following way: The cloth is first soaked in a solution of an aluminium salt. It is then exposed to the action of steam, whereby the aluminium salt is completely hydrolyzed, the resulting aluminium hydroxide being thus thoroughly incorporated in the fiber. If the cloth is now dipped into a solution of the dye, the aluminium hydroxide combines with or absorbs the color substance and fastens, or "fixes," it upon the fiber. A substance such as aluminium hydroxide which serves this purpose is known as a *mordant*.

The compounds which serve well as mordants may be precipated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes*.

Aluminium chloride ($AlCl_3$). The anhydrous chloride, which is used in the synthesis of many carbon compounds, is made by heating aluminium turnings in a current of chlorine. The hydrated chloride, $AlCl_3 \cdot 6\,H_2O$, is prepared by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. When heated it is converted into the oxide, resembling magnesium chloride in this respect:

$$2\,(AlCl_3 \cdot 6\,H_2O) \longrightarrow Al_2O_3 + 6\,HCl + 9\,H_2O$$

Aluminium sulfate, $Al_2(SO_4)_3$. This compound is prepared by the action of sulfuric acid on bauxite or one of the common silicates of aluminium. It crystallizes from water under ordinary conditions as $Al_2(SO_4)_3 \cdot 18\,H_2O$. It is cheapest of the soluble salts of aluminium and is used in the purification of water, in the preparation of alums, and in certain processes connected with dyeing or with the manufacture of paper.

Alums. Aluminium sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow 2\,(KAl(SO_4)_2 \cdot 12\,H_2O)$$

The sulfates of other trivalent metals can form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminium. They all crystallize in octahedra and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

Potassium alum	$KAl(SO_4)_2 \cdot 12\,H_2O$
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12\,H_2O$
Ammonium iron alum	$NH_4Fe(SO_4)_2 \cdot 12\,H_2O$
Potassium chrome alum	$KCr(SO_4)_2 \cdot 12\,H_2O$

Very large well-formed crystals of an alum can be prepared by suspending a small crystal by a thread in a saturated solution of the alum, as shown in Fig. 181. The small crystal slowly grows and often assumes a very perfect form.

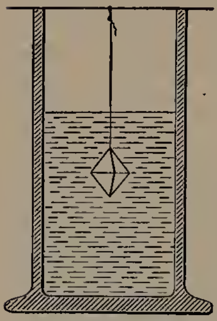


FIG. 181. Growing a perfect crystal of alum

Hydrolysis of salts of aluminium. While aluminium hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (p. 226). Thus, when an aluminium salt and a soluble carbonate are brought together in solution, we should expect to have aluminium carbonate precipitated according to the equation

$$3\,Na_2CO_3 + 2\,AlCl_3 \longrightarrow Al_2(CO_3)_3 + 6\,NaCl$$

But if it is formed at all, it instantly begins to hydrolyze, the products of the hydrolysis being aluminium hydroxide and carbonic acid, the latter then forming carbon dioxide and water:

$$Al_2(CO_3)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2CO_3$$
$$3\,H_2CO_3 \longrightarrow 3\,H_2O + 3\,CO_2$$

It is because of these reactions that alum is used as a constituent of some baking powders.

Baking powders. Mixtures of sodium bicarbonate, flour (or starch), and some substance that will act upon the bicarbonate to liberate carbon dioxide are known as *baking powders.* They are used as aërating agents in preparing such foods as cakes and biscuits, the carbon dioxide evolved pushing its way through the dough and rendering it porous and light. The compounds commonly employed for liberating the carbon dioxide from the sodium bicarbonate are either alum, cream of tartar (potassium bitartrate), or calcium hydrogen phosphate, and baking powders are known as *alum baking powders*, *cream of tartar baking powders*, or *phosphate baking powders*, according to whether they contain the one or other of these constituents. The reactions take place only in the presence of water; hence the use of the flour, which, by absorbing any moisture that may be present, prevents the powder from losing its strength until used. In place of alum a mixture of sodium sulfate and aluminium sulfate known as cream of tartar substitute, or simply as C. T. S., is largely used. The complete reaction that takes place when water is added to an alum baking powder is somewhat complex, but it amounts to the formation of aluminium carbonate, which hydrolyzes as fast as formed, evolving carbon dioxide, as explained in the preceding paragraph.

Aluminium nitride (AlN). This compound is prepared by the direct union of aluminium and nitrogen at a high temperature. It derives its chief interest from the fact that, when it is treated with steam, ammonia is formed.

$$2\,AlN + 3\,H_2O \longrightarrow Al_2O_3 + 2\,NH_3$$

The nitrogen used in preparing the nitride is obtained from the air. It is possible, therefore, through the intermediate formation of aluminium nitride to convert the nitrogen from the air into ammonia.

The utilization of atmospheric nitrogen. Repeated attempts have been made to utilize the inexhaustible supplies of free nitrogen present in the atmosphere, by converting the nitrogen into useful compounds, especially ammonia, nitric acid, and nitrates. A number of different methods for accomplishing this end have been discussed in their appropriate connections; it is desirable to collect these together under one heading.

1. The nitrogen may be converted into calcium cyanamide. This may be used directly as a fertilizer or it

may be converted into ammonia or sodium cyanide as explained on page 433.

2. The nitrogen may be converted into ammonia. This is accomplished by heating nitrogen and hydrogen under the proper conditions (p. 203).

3. The nitrogen may be converted into aluminium nitride and ammonia prepared from this as described above.

4. The nitrogen may be converted into nitric acid. This is effected by sparking mixtures of nitrogen and oxygen and conducting the resulting oxides into water as described on page 208.

At present it is cheaper to prepare ammonia from coal and nitric acid from Chile saltpeter. Nevertheless, it is certain that increasing amounts of these compounds will be prepared from atmospheric nitrogen as time goes on.

EXERCISES

1. What metals and compounds studied are prepared by electrolysis?

2. Write the equation for the reaction between aluminium and hydrochloric acid; between aluminium and sulfuric acid.

3. What hydroxides have we studied that have both acid and basic properties? What are such hydroxides called?

4. Write equations showing the methods used for preparing aluminium hydroxide and aluminium sulfate.

5. Write the general formula of an alum, representing an atom of a univalent metal by X and an atom of a trivalent metal by Y.

6. What is the significance of the term *colloid* as applied to aluminium hydroxide?

7. Compare the properties of the hydroxides of the different groups of metals so far studied.

8. In what respects does aluminium oxide differ from calcium oxide in properties?

9. Where should you expect the factories for the production of aluminium to be located?

10. Why do the directions for using aluminium cooking utensils state that such utensils must not be washed in alkaline solutions?

11. Aluminium sulfide is completely hydrolized by water. Write the equations for the reactions you would expect to take place when a solution of ammonium sulfide is added to a solution of aluminium chloride.

12. What is the aërating agent used in the making of bread? Why not use baking powder?

13. A mixture of sour milk and sodium bicarbonate is sometimes used as an aërating agent in place of baking powder. What is the chemistry involved?

14. What is the derivation of the word *mordant*? (Consult dictionary.)

15. Give four different ways in which nitrogen from the atmosphere can be converted into nitric acid.

16. 1 kg. of potassium alum contains what weight of water of hydration?

17. A certain bauxite ore was found to contain 90 per cent of $Al_2O_3 \cdot 3\,H_2O$. What weight of aluminium could be obtained from 1 ton of the ore?

CHAPTER XXXVII

ALUMINIUM SILICATES AND THEIR COMMERCIAL APPLICATIONS

Aluminium silicates. One of the most common constituents of rocks is feldspar ($KAlSi_3O_8$), a mixed salt of potassium and aluminium with the condensed silicic acid, $H_4Si_3O_8$. Under the influence of moisture, carbon dioxide, and changes of temperature this substance is constantly being broken down into soluble potassium compounds and aluminium silicate ($Al_2Si_2O_7 \cdot 2\,H_2O$). In relatively pure condition the latter is called *kaolin* and is a soft, plastic mineral; in the impure state, mixed with sand and other substances, it forms common *clay*. *Mica* is another very abundant mineral, having a varying composition, but being essentially of the formula $KAlSiO_4$. *Serpentine*, *talc*, *asbestos*, and *meerschaum* are important complex silicates of aluminium and magnesium; *granite* is a mechanical mixture of silica, feldspar, and mica and is therefore rich in aluminium. *Fuller's earth* is a peculiar form of aluminium silicate, which is used as a filtering material for decolorizing oils, especially cottonseed oil.

Clay products. The crudest forms of clay products, such as porous brick and draintile, have little chemistry involved in their manufacture. Natural clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless iron compounds in the clay are converted into colored compounds which give the usual red color to these articles. In making *vitrified brick* the temperature is raised to the point at which fusion begins, so that the brick is partially changed to a kind of glass.

White pottery. This term is applied to a variety of articles ranging from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads; namely, (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

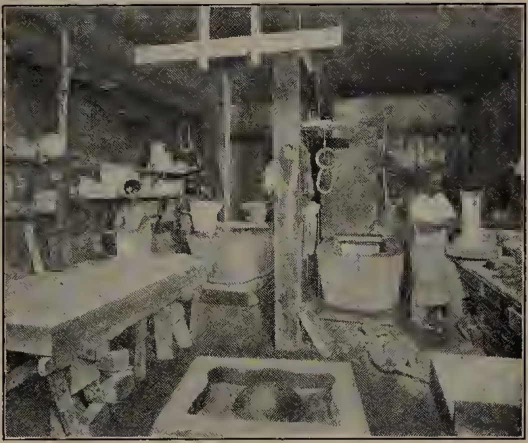


FIG. 182. The manufacture of pottery: molding the plastic material into form

The body of the ware. The materials used consist of clay artificially prepared from kaolin, plastic clay, and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel (Fig. 182). The ware is then dried and burned in a kiln (Fig. 183) until vitrified, and in this form is known as *bisque*. This is usually porous and must therefore be glazed to render it nonabsorbent and give it a smooth surface.

The glaze. The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are silica, feldspar, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste.

The bisque is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

The decoration. If the article is to be decorated, the design may be painted upon the body before the article is glazed, or it may be painted upon the glaze and the article fired again, the pigments melting into the glaze. In the former case the pigments used are as a rule metallic oxides of various colors, while in the latter case they are often colored glasses.

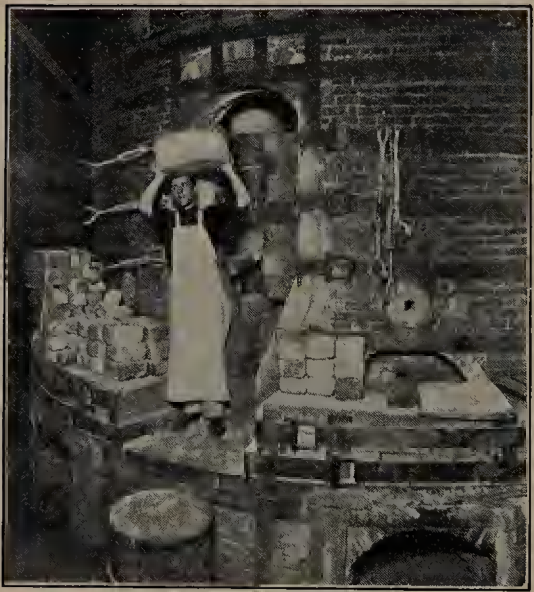


FIG. 183. The manufacture of pottery: stacking the ware in the kiln for firing

Cement. The term *cement* as ordinarily used at present is applied to those mortars which possess the property of hardening in water as well as in air. These cements are silicate bodies, usually very highly basic in character, and when ground fine and mixed with water they undergo complex reactions resulting in the formation of a hard, rock-like mass. A number of different classes of cements are known, the most important of which is called *Portland* cement.

Composition of Portland cement. The essential ingredients of Portland cement and their percentages are as follows:

SiO_2	19 to 26%	MgO	0 to 5%
Al_2O_3	4 to 11%	SO_3	0 to 2.5%
Fe_2O_3	2 to 5%	Na_2O K_2O	0 to 3%
CaO	58 to 67%		

Manufacture of Portland cement. The materials most commonly employed are limestone or marl and clay or shale. In general, however, any substance may be used which furnishes the ingredients listed in the above table. Among the substances so used is blast-furnace slag, which is an impure calcium-aluminium silicate.

The materials to be used are coarsely ground and then mixed together in the proper proportions and finely pulverized. The resulting mixture is run into a furnace and burned to a temperature just short of fusion, at which temperature it vitrifies, forming a grayish mass known as *clinker*. Finally, the clinker is ground to a fine powder. Gypsum is often added in the process; this acts as a negative catalyzer, retarding the hardening, or setting, of the cement.

Fig. 184. A bridge built of reënforced concrete

The setting of cement. The reactions which take place upon the addition of water to cement and which result in the formation of a hard, rocklike mass are not thoroughly understood. The constituents of the cement apparently undergo hydrolysis when they come in contact with water. The resulting compounds unite with water, producing hydrates. These hydrates are crystalline in character and form a hard, compact mass.

Growing importance of cement. Cement is rapidly coming into use for a great variety of purposes. It is often used in place of mortar in the construction of brick buildings. Mixed with crushed stone and sand it forms *concrete*, which is used in foundation work for buildings and street paving. It is also used in making artificial stone, terra-cotta trimmings for buildings, artificial-stone walks and floors, fence posts, and the like. It is being used more and more for making articles which were formerly made of wood or stone, and the entire walls of buildings are sometimes made of cement blocks or concrete. Iron rods or wire are often embedded in the concrete before it sets, to give it greater strength, and this is called *reënforced concrete.*

EXERCISES

1. In the manufacture of pottery why is the glaze made more fusible than the body of the ware?

2. Suppose that the glaze and the body expand and contract at different rates with changes in temperatures, what will be the result?

3. What is the meaning of the word *vitrify*?

4. What is a catalyzer? What is a *negative* catalyzer?

5. Why can cement be used as mortar in colder weather than ordinary mortar?

6. What is meant by a condensed acid? Give example.

7. What weight of kaolin will result from the weathering of 1 ton of feldspar?

CHAPTER XXXVIII

THE IRON FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	OXIDES
Iron	Fe	55.84	7.86	1530°	FeO, Fe_2O_3
Cobalt	Co	58.97	8.6	1480°	CoO, Co_2O_3
Nickel	Ni	58.68	8.9	1452°	NiO, Ni_2O_3

The family. The elements iron, cobalt, and nickel bear a relation to one another which is different from that existing among the members of any other family as yet considered. Their atomic weights are very close together, and in the periodic table they are placed in one family not because the plan of arrangement brings them together but because they are so similar (p. 256) and evidently constitute a natural family.

The elements occur in nature chiefly as oxides and sulfides, though they have been found in very small quantities in the native state, usually in meteorites. Of the three iron is by far the most abundant, cobalt and nickel being of rather rare occurrence. Iron and nickel find commercial uses chiefly in metallic form, while cobalt is more widely used in the form of compounds. Their sulfides, carbonates, and phosphates are insoluble in water, the other common salts being soluble. Their salts are usually highly colored, those of iron being yellow or light green as a rule, those of nickel darker green, while cobalt salts are usually rose colored.

IRON

Occurrence. The element iron has long been known, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure condition. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, very few rocks or soils are free from small percentages of iron. It is a constituent of the chlorophyll of plants and the hæmoglobin of the blood of animals, and therefore plays an important part in life processes. Many meteorites are largely iron, usually alloyed with a little nickel.

Pure iron. Pure iron may be prepared by the electrolysis of a solution of iron sulfate between iron electrodes, though it is difficult to free it entirely from hydrogen in this way. Hydrogen from the water of the electrolyte is liberated at the cathode along with the iron and is dissolved, or *occluded*, in the iron as the latter deposits. Iron is prepared in practically pure condition by the open-hearth method (p. 478). It is a silvery metal which melts at 1530°. It is ductile and malleable and almost as soft as aluminium. It is especially well adapted to the manufacture of electromagnets, since it acquires and loses magnetic properties more readily than do the ordinary varieties of iron. It is also used for purposes where resistance to corrosion is desired, for it does not rust rapidly.

The iron of commerce. Iron differs from most of the other metals used in the industries in that the pure metal is seldom obtained and is of limited application, while that containing small percentages of other elements exhibits a wide variety of properties which make it of the greatest value for many different purposes.

Carbon is always present in amounts which vary from a mere trace to about 7 per cent. According to the condition of treatment the carbon may be in the form of graphite scattered through the iron, or it may occur as a solid solution of carbon in iron, or as carbides of iron. One of these carbides has the formula Fe_3C and is called *cementite.* Manganese, silicon, and traces of phosphorus, sulfur, and oxygen are also present.

The properties of the iron are so much modified by the percentages of these elements, by their form of combination, and by the treatment of the metal during its production, that many varieties of iron are recognized in commerce, the chief of which are *cast iron*, *wrought iron*, and *steel.*

The metallurgy of iron. The problem to be solved in the production of commercial iron is (1) to obtain a metallic alloy of the requisite chemical composition and physical properties and (2) to produce it on a very large scale. The development of the huge modern furnaces has demanded a wonderful application of chemical knowledge to a definite purpose and a no less wonderful engineering skill in securing the present great scale of production. To understand the processes to be described it will be necessary to remember constantly that large and rapid production is fully as necessary as great purity.

Materials used in metallurgy of iron. Four different classes of materials are used in the metallurgy of iron:

1. ***Iron ore.*** The ores most frequently employed are the following:

Hematite	Fe_2O_3	Siderite . . .	$FeCO_3$
Magnetite	Fe_3O_4	Limonite . .	$2\,Fe_2O_3 \cdot 3\,H_2O$

As mined for use all ores contain earthy matter and often sulfides and phosphates as well.

While iron ore is mined in a number of different localities in the United States, the great center of production is in the neighborhood of Lake Superior, the ore being chiefly *hematite.* Fig. 185 represents one of the large mines in Minnesota. Large amounts are also mined near Birmingham, Alabama.

2. ***Carbon.*** Carbon in some form is necessary both as a *fuel* and as a *reducing agent.* In former times wood charcoal was used to supply the carbon, but now coke is almost universally used.

Fig. 185. Mining iron ore in Minnesota

3. ***Hot air.*** To maintain the high temperature that is required for the reduction of iron, a very active combustion of fuel is necessary. This is secured by forcing a strong blast of *hot air* into the lower part of the furnace during the reduction process.

4. ***Flux.*** All the materials which enter the furnace must leave it again, either in the form of gases or as liquids. The *iron* is drawn off as the liquid metal after its reduction, the *oxygen* with which it was combined escaping as oxide of carbon. To secure the removal of the *earthy matter* charged into the furnace along with the ore, materials are added to the charge which will combine with the impurities in the ore, forming a liquid. The material added for this purpose is called the *flux*, and the liquid produced from the flux and the ore is called *slag.*

The slag. The slag is a variety of difficultly fusible glass, being essentially a calcium-aluminium silicate. If the ore is rich in silica, as is usual, limestone is used as a flux; if the ore contains limestone, silica or feldspar is used; if the ore is very pure, both constituents must be added as flux.

The formation of slag converts the oxides of calcium, magnesium, aluminium, and silicon contained in the ore into the liquid state, and not only does this make the removal of these materials easy, but the liquid is a necessity for other reasons. It is a medium in which the little droplets of iron run together into one large mass; it keeps the contents of the furnace fused and so prevents clogging; it floats over the collected iron and prevents its oxidization. In every operation in which iron is melted a slag must be provided.

Cast iron. Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron.* The ores are mixed with a suitable flux, and are reduced by heating with coke.

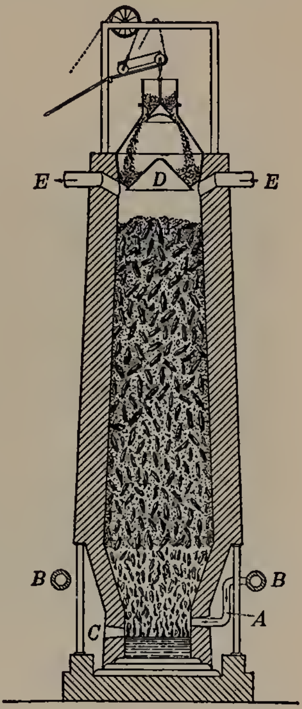


FIG. 186. Vertical section of a blast furnace

Blast-furnace process. The reduction is carried out in a large tower called a blast furnace (Fig. 186). This is usually 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes (*A*) called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe (B) which girdles the furnace. At the base of the furnace is an opening, through which the liquid metal can be drawn off from time to time. There is also a second opening (C) somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap (D) called the *bell*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through pipes E. These gases are very hot and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères and as fuel for the engines.

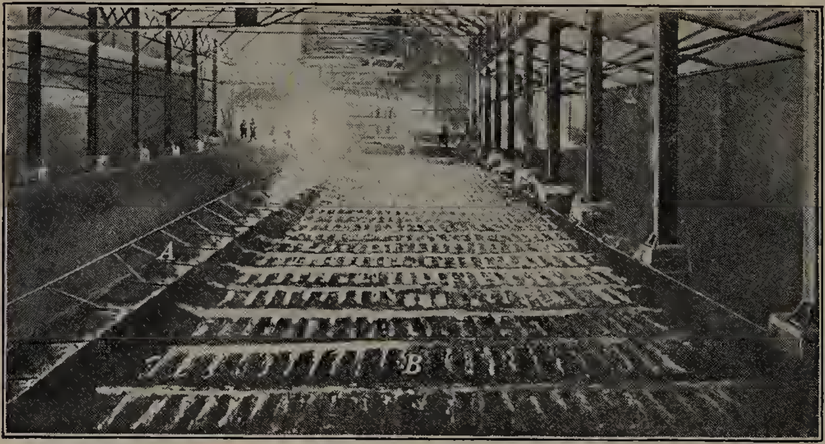


FIG. 187. Casting pig iron from a blast furnace

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the bell. The coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends the reduction is completed, and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has collected, the slag is drawn off through C, and the iron is run into ladles and taken to the *steel furnaces* for the manufacture of steel, or it is run into sand molds and cast into ingots called *pigs*. Fig. 187 shows the method of drawing off the iron. A small hole is made near the bottom of the furnace, and the molten iron flows out and down the central channel A and into the sand molds along the sides B, where it solidifies.

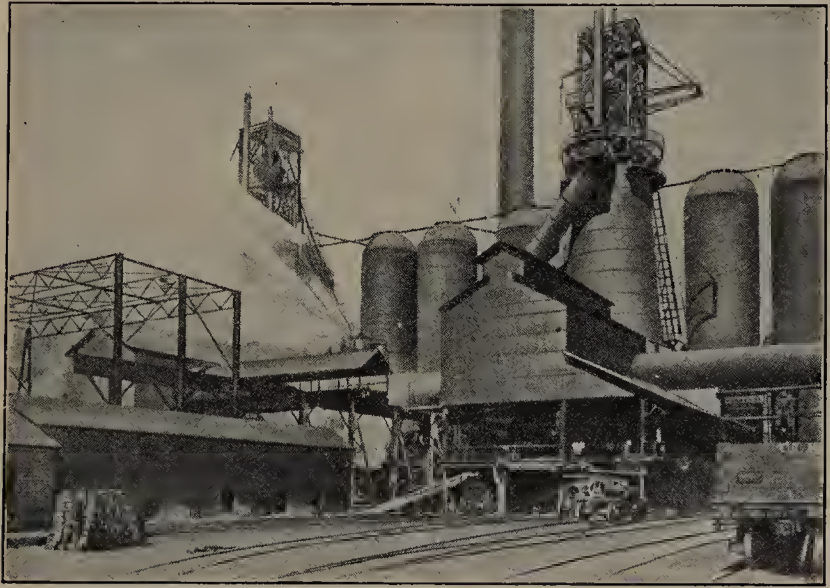


Fig. 188. A typical plant for the manufacture of cast iron

In practice a number of furnaces are usually operated together, as illustrated in Fig. 188, which shows an exterior view of a modern plant for making cast iron.

Properties of cast iron. The iron produced in the blast furnace is called *cast iron.* It varies considerably in composition, but always contains over 2 per cent of carbon, variable amounts of silicon, and at least traces of phosphorus and sulfur. The form in which the carbon is present, whether free or combined, also greatly modifies the properties of the iron. In general, cast iron is hard and brittle, and melts at about 1150°. It cannot be welded or forged, but is easily cast in sand molds. It is rigid, but not elastic, and its tensile strength is small. It is used for making castings, but chiefly as a starting point in the manufacture of other varieties of iron.

Wrought iron. Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur, the operation being conducted in what is called a *puddling furnace.*

Fig. 189. Vertical section showing details of a Bessemer converter

Wrought iron is soft, malleable, and ductile. Its tensile strength is greater than that of cast iron, but less than that of most steel. Its melting point is much higher than that of cast iron. If melted, it is changed into steel. It is no longer produced to the same relative extent as in former years, since soft steel can be made at a less cost and is well adapted to almost all the uses for which wrought iron was used. Its chief use is in making materials subject to corrosion, such as water pipes.

Steel. Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are quite different from that employed in the manufacture of wrought iron. Nearly all the steel of commerce produced in the United States is made by one of two general methods known as the *acid Bessemer process* and the *basic open-hearth process.*

Acid Bessemer process. In the acid Bessemer process the furnaces used are lined with *silica,* which, it will be recalled, is an *acid anhydride.* These furnaces remove from the cast iron the carbon and silicon, but not the phosphorus and sulfur. The process is therefore employed when the cast iron to be used is low in phosphorus and sulfur.

Details of operation of Bessemer process. This process, invented about 1880, is carried out in great egg-shaped crucibles called *converters* (Fig. 189), each one of which will hold as much as 15 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber (*A*), which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

FIG. 190. The brilliant flame of a Bessemer converter

White-hot liquid cast iron from a blast furnace is run into the converter through its open, necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on, and the converter is rotated to a nearly vertical position. The carbon manganese and silicon in the iron are rapidly oxidized (first the silicon and manganese and then the carbon), the oxidation being attended by a brilliant flame (Fig. 190). The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires on the average about ten minutes, and when it is complete the desired quantity of carbon (generally in the form of high-carbon iron alloy) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects. The process must be conducted very rapidly, for as soon as the silicon and carbon have been burned there is no way to keep the iron from cooling, and it must be poured at once.

Basic open-hearth process. In the basic open-hearth process the lining of the furnace is made of limestone or dolomite, both of which act as *bases*. In such furnaces the phosphorus and sulfur are both removed, as well as the silicon and carbon. The presence of more than traces of phosphorus and sulfur in the finished steel renders the metal so brittle that it is worthless for most purposes. The open-hearth process, therefore, possesses a great advantage over the acid Bessemer process in that it makes it possible to utilize iron ores (or cast iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced.

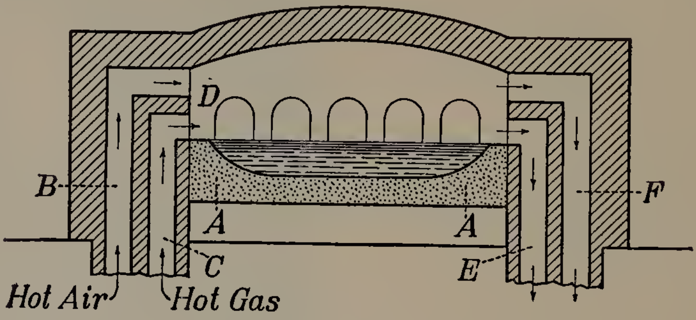


Fig. 191. Vertical section of an open-hearth furnace

Details of the open-hearth process. Fig. 191 shows the simpler parts of the type of furnace used in this process. The hearth of the furnace is about 40 ft. in length, 12 ft. in width, and 2 ft. in depth, and is lined with limestone or dolomite (*A*, *A*).

Either gas or sprayed oil is used as fuel and finely powdered coal is now being employed. Below the furnace is placed a checkerwork of brick so arranged that the hot products of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased.

The gas entering through *C* comes in contact at *D* with the hot air entering through *B*, and a vigorous combustion results, the flame passing above and over the cast iron and lime with which the furnace is charged. The products of combustion escape through *E* and *F*. At the temperature reached, the carbon in the cast iron is removed in the form of the oxide, the escaping gas giving the melted metal the appearance of boiling. The silicon, phosphorus, and sulfur unite with oxygen to form acid anhydrides; these combine with the lime to form a slag, and this rises to the surface of the melted charge and is easily removed.

When a test shows that the desired percentage of carbon is present the melted steel is run into large ladles and then into molds. An average furnace produces about 50 tons of steel in a given charge, approximately eight hours being required in the process. At present by far the largest amount of steel produced in the United States is made by this process.

Tool steel or crucible steel. Steel designed for use in the manufacture of edged tools and similar articles should be relatively free from silicon and phosphorus, but should contain from 0.5 to 1.5 per cent of carbon. The percentage of carbon should be regulated by the exact use to which the steel is to be put. Steel of this character is usually made in small lots from either Bessemer or open-hearth steel in the following way.

A charge of melted steel is placed in a large crucible and the calculated quantity of pure carbon is added. The carbon dissolves in the steel, and when the solution is complete the metal is poured out of the crucible. This is sometimes called crucible steel.

Electrothermal metallurgy of steel. An increasing quantity of high-grade tool steel is being produced in electrical furnaces. The furnace is heated by electrical energy, and a large quantity of steel can be kept melted in these furnaces as long as may be desired. The electrical current is used merely to produce heat, so that the process is not dependent upon electrolysis. This method is almost identical with the open-hearth method, save in the way in which the heat is supplied, and produces the same kind of steel as does the latter method.

Properties of steel. Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, and not more than traces of phosphorus and sulfur. When desired, a product containing as high as 99.85 per cent of iron can be produced by the open-hearth method. Such steel is very soft, but resists rust. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel can be rolled into sheets, cast in molds, and forged into desired shapes.

The hardening and tempering of steel. When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then allowed to cool slowly this hardened steel becomes softer and less brittle, and this process is known as *tempering.*

By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any condition of hardness demanded for a given purpose, as for making springs or cutting-tools. Steel assumes different color tints at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures for the tempering of tools:

220°	paper cutters, wood-engraving tools
240°	knife blades, rock drills
260°	hand-plane cutters and cooper's tools
275°	axes, springs
290°	needles, screw drivers
300°	wood saws

Alloy steels. As we have seen (p. 475), small quantities of carbon greatly modify the properties of iron, and equally marked effects may be produced by a great many other elements. Accordingly, to secure a steel with the requisite properties, suitable percentages of these elements are added to the steel just before it is run out of the furnace. The elements most frequently added are manganese, silicon, nickel, chromium, tungsten, vanadium, and titanium, and steel containing an appreciable percentage of any of these elements is called an *alloy steel.* The alloy element is added in the form of a rich alloy of iron, such as *ferrochromium* or *ferromanganese.*

The approximate percentage of metals other than iron present in some of the principal steel alloys, as well as the chief uses of the alloys, is as follows:

3.5% nickel	armor plate, nickel steel
3.5% nickel and 2.5% chromium	armor plate and projectiles
12.0% manganese	burglar-proof safes
5.0% chromium and from 8 to 24% tungsten	high-speed lathe tools
0.1% titanium	car rails and steel castings
0.2% vanadium, 3.5% nickel, 0.75% chromium and 0.4% manganese	automobile springs and axles
12–15% silicon (duriron and tantiron)	retorts for distilling acids, electrodes

Steel purifiers. The great difficulty in securing a good steel is (1) to accomplish the complete reduction of the oxide and (2) to prevent the absorption of gases which cause blowholes as the casting solidifies. These difficulties are avoided, as far as possible, by adding to the steel, at the close of the operation, certain elements which will combine with the oxygen and the absorbed gases. The compounds formed pass into the slag, and almost none of the added element remains in the finished product. Aluminium is used to a large extent for this purpose, as are also vanadium and titanium. Such elements are called *purifiers* or *scavengers*.

Compounds of iron. Iron differs from the metals so far studied, in that it is able to form *two series* of compounds. In the one series the iron is *bivalent* and forms compounds which in formulas and many chemical properties are similar to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *trivalent* metal and forms salts similar to those of aluminium. These salts are known as *ferric* compounds.

Oxides of iron. Iron forms several oxides. Ferrous oxide (FeO) is not found in nature, but can be prepared artificially in the form of a black powder which easily takes up oxygen, forming ferric oxide:

$$4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3$$

Ferric oxide is the most abundant ore of iron and occurs in great deposits, especially in the Lake Superior region. It is found in many mineral varieties which vary in density and color, the most abundant being *hematite*, which ranges in color from red to nearly black. When prepared artificially it is a bright-red powder which is used as a pigment (*Venetian red*) and as a polishing powder (*rouge*).

Magnetite has the formula Fe_3O_4 and is a combination of FeO and Fe_2O_3. It is a very valuable ore, but is less abundant than hematite. It is sometimes called magnetic oxide of iron, or *loadstone.*

Ferrous salts. These salts are obtained by dissolving iron in the appropriate acid or, when they are insoluble, by precipitation. The crystallized salts are usually light-green in color and are hydrates. Ferrous hydroxide is a base of about the same strength as the hydroxide of zinc or of magnesium. Consequently ferrous salts are not very much hydrolized in solution.

Ferrous sulfate ($FeSO_4$). Ferrous sulfate is the most familiar ferrous compound. It is usually obtained in the form of the hydrate $FeSO_4 \cdot 7\,H_2O$, called *copperas,* or *green vitriol,* and is prepared commercially as a by-product in the steel-plate mills. Preparatory to galvanizing or tinning (p. 447), steel plates are cleaned by immersing them in dilute sulfuric acid, and in the process some of the iron dissolves. The liquors are concentrated, and the green vitriol separates from them. The salt is used in the manufacture of ink and of iron alum, as a substitute for aluminium sulfate in the purification of water, and as a reagent to destroy weeds.

Ferrous sulfide (FeS). Ferrous sulfide is sometimes found in nature as a golden-yellow crystalline mineral called *pyrrhotite.* It is formed as a black precipitate when a soluble sulfide and an iron salt are brought together in solution :

$$FeSO_4 + Na_2S \longrightarrow FeS + Na_2SO_4$$

It can also be made as a heavy dark-brown solid by fusing together the requisite quantities of sulfur and iron. It is used in the laboratory in the preparation of hydrogen sulfide (p. 233).

Iron disulfide (pyrite) (FeS_2). This substance occurs abundantly in nature in the form of brass-yellow cubical crystals and in compact masses. Sometimes it is called *fool's gold* from its superficial resemblance to the precious metal. It is used in very large quantities as a source of sulfur dioxide in the manufacture of sulfuric acid, since it burns readily in the air, forming ferric oxide and sulfur dioxide:

$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$

Ferrous carbonate ($FeCO_3$). This compound occurs in nature as *siderite* and is a valuable ore. Like calcium carbonate, it dissolves to some extent in water containing carbon dioxide, forming the more soluble acid carbonate:

$$FeCO_3 + H_2CO_3 \rightleftarrows Fe(HCO_3)_2$$

Spring waters containing acid carbonate in solution are called *chalybeate* waters.

Ferric salts. The crystallized ferric salts are usually yellow or violet in color. In solution and in the absence of free acid they hydrolyze even more readily than the salts of aluminium. This fact indicates that ferric hydroxide, $Fe(OH)_3$, is a very weak base.

Ferric hydroxide, $Fe(OH)_3$. When solutions of ferric salts are treated with ammonium hydroxide, ferric hydroxide is formed as a rusty-red precipitate insoluble in water. It might be thought that this same precipitate would form when ferric salts undergo hydrolysis in solution,

$$FeCl_3 + 3\,H_2O \longrightarrow Fe(OH)_3 + 3\,HCl$$

but as a rule no precipitate forms, because the ferric hydroxide remains in the form of a colloid. If the solution is boiled, some of this colloid is coagulated as a precipitate.

Iron *rust* is a variable mixture of hydrated oxides of iron. When a film of rust forms on iron it does not protect the metal from the further action of water as does the rust of aluminium and zinc, because iron rust is porous and also tends to scale off, exposing a fresh surface.

The rusting of iron. A number of different theories have been advanced to account for the changes taking place in the rusting of iron. The most satisfactory of these is known as the electrolytic theory. According to this the primary reaction in the rusting of iron is between iron and water, as expressed in the following equation:

$$Fe + 2\,(H^+,\ OH^-) \longrightarrow Fe^{++},\ 2\,OH^- + H_2$$

The ions Fe^{++} and $2\,OH^-$ then combine to form ferrous hydroxide, $Fe(OH)_2$. This is further acted upon by oxygen and water, and forms the complex substance known as iron rust. It is evident that the composition of rust will vary according to the conditions of its formation.

Ferric chloride ($FeCl_3$). This salt is the most familiar of the ferric salts. It can be obtained most conveniently by dissolving iron in hydrochloric acid and then passing chlorine into the solution:

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$$
$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

The salt when crystallized from water has the formula $FeCl_3 \cdot 6\,H_2O$.

Oxidation of ferrous salts. A ferrous salt in solution, exposed to the action of the air or of an oxidizing reagent, is rapidly converted into a ferric salt by oxidation. For example, in the presence of hydrochloric acid the oxidation of ferrous chloride takes place, as follows:

$$2\,FeCl_2 + [O] + 2\,HCl \longrightarrow 2\,FeCl_3 + H_2O$$

In the absence of free acid the reaction is somewhat more complicated, but is of the same order.

It will be seen that the valence of the iron atoms has been increased from 2 to 3. This increase is always called oxidation even in cases in which no oxygen is concerned, (p. 31) as is illustrated in the equation

$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

This latter equation may be written in such a way as to show the change in the electrical charges upon the ions:

$$2\,(Fe^{++}, Cl^-, Cl^-) + Cl_2 \longrightarrow 2\,(Fe^{+++}, Cl^-, Cl^-, Cl^-)$$

The charge upon each cation (Fe^{++}) has been increased from 2 to 3, and a corresponding number of anions have been formed. In general, *the term oxidation is applied to all reactions in which the valence of a metallic cation is increased.*

Reduction of ferric salts. The changes that take place when a ferric salt is exposed to the action of nascent hydrogen or other reducing agents, such as metals, are the reverse of the ones just described. This is seen in the following equations:

$$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$$
$$2\,FeCl_3 + Zn \longrightarrow 2\,FeCl_2 + ZnCl_2$$

In these reactions the valence of the iron atoms has been lowered from 3 to 2. These equations may also be written in a form to show the change of charge upon the cations (Fe^{+++}):

$$(Fe^{+++}, Cl^-, Cl^-, Cl^-) + [H] \longrightarrow (Fe^{++}, Cl^-, Cl^-) + (H^+, Cl^-)$$

Although no oxygen has been removed, the ferric chloride is said to be *reduced* (p. 48). In general *when the valence of a metallic cation is diminished the salt is said to be reduced.*

Sodium ferrocyanide ($Na_4FeC_6N_6$); potassium ferrocyanide ($K_4FeC_6N_6$). These compounds are salts of the unstable hydroferrocyanic acid, $H_4FeC_6N_6$. They are prepared from by-products obtained in the manufacture of coke. When the coal is heated in the absence of air small amounts of the carbon, nitrogen, and hydrogen present are evolved in the form of hydrogen cyanide. This is absorbed and converted into calcium ferrocyanide by means of calcium hydroxide and the spent iron oxide employed in the purification of the gas evolved in the coking of the coal. The calcium ferrocyanide so obtained is converted into sodium or potassium ferrocyanide by treatment with appropriate salts of sodium or potassium. The reactions involved in the complete process are quite complex.

Both sodium ferrocyanide and potassium ferrocyanide are yellow in color and are readily soluble in water. The latter compound is often called *yellow prussiate of potash.* The sodium salt crystallizes from water in the form of the hydrate $Na_4FeC_6N_6 \cdot 10\,H_2O$, while the potassium salt crystallizes as the hydrate of $K_4FeC_6N_6 \cdot 3\,H_2O$. In solution they ionize as follows:

$$Na_4FeC_6N_6 \longrightarrow 4\,Na^+ + FeC_6N_6^{----}$$
$$K_4FeC_6N_6 \longrightarrow 4\,K^+ + FeC_6N_6^{----}$$

It is important to notice that no ions of iron are present, so that these salts do not give the ordinary reactions for iron. They react with ferric salts such as ferric chloride in accordance with the following equation:

$$3\,K_4(FeC_6N_6) + 4\,FeCl_3 \longrightarrow Fe_4(FeC_6N_6)_3 + 12\,KCl$$

The resulting ferric ferrocyanide is a blue insoluble solid and is ordinarily called *Prussian blue.* It is a common paint pigment, and most of the ferrocyanides made are used in the preparation of this pigment.

Potassium ferricyanide ($K_3FeC_6N_6$). By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are deposited which have the composition $K_3FeC_6N_6$:

$$2\,K_4FeC_6N_6 + Cl_2 \longrightarrow 2\,K_3FeC_6N_6 + 2\,KCl$$

This compound is called potassium ferricyanide, or *red prussiate of potash.*

In place of chlorine one may use nascent oxygen evolved by electrolysis. It is only necessary to electrolyze a solution of potassium ferrocyanide in water. The oxygen evolved at the anode converts the potassium ferrocyanide into the ferricyanide.

Blue printing. When a ferric salt and potassium ferricyanide are brought together in solution no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to a ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of *blue printing.* A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used) and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, during which process the portions acted upon by the light turn blue, while the unaffected portions are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blue print, since this base decolorizes Prussian blue.

Other salts of iron. The following compounds of iron have industrial uses:

Ferric sulfate, $Fe_2(SO_4)_3$	a white solid
Ferric nitrate, $Fe(NO_3)_3 \cdot 6\,H_2O$	violet crystals
Iron alum, $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$ . . .	violet crystals

Inks. Many of the common black inks are made by treating an extract of *nutgalls* with ferrous sulfate and adding a blue-black dye. The nutgalls are rich in *tannic acid*, and this, with ferric compounds formed by the oxidation of the ferrous sulfate by the air, gives a nearly black precipitate. The black dye gives a temporary color, the permanent color being developed after the writing has been exposed to the air. The addition of some colloidal material, such as gum arabic or dextrin, together with a little sulfuric acid, delays the precipitation of the black substance in the bottle. A preservative is usually added to prevent the ink from molding. Formerly all black inks were made by the above method. At present aniline dyes are being used more and more for making such inks.

COBALT AND NICKEL

Occurrence. Cobalt and nickel are almost always found together in ores which also contain iron, silver, and copper, in combination with arsenic and sulfur. The richest deposits are in Ontario and New Caledonia. The extraction of these metals from their ores and their separation from each other is too complicated a process to be described here. Nickel is also a frequent impurity of crude copper, and several million pounds of nickel sulfate are annually recovered in the United States in the refining of copper by electrolysis.

Properties and uses. Both these metals are silvery in appearance and take a high polish. They are somewhat heavier than iron, and melt at a lower temperature. Their chief use is in making alloys. An alloy of cobalt and chromium is used for making cutlery and lathe tools. Nickel coinage consists of 75 per cent of copper and 25 per cent of nickel. German silver (p. 497) also contains about 25 per cent of nickel. Nickel steel usually contains about 3.5 per cent of nickel, and prior to the war more than half of the nickel produced was used in making this product. Invar contains about 36 per cent of nickel and does not expand when heated. Monel metal is an alloy consisting of 60 per cent of nickel, 33 per cent of copper, and 6.5 per cent of iron, and it possesses very great tensile strength. Modern rifle bullets are made of an alloy of copper and nickel of about the composition of Monel metal. They are as hard as steel and much heavier. Nickel is extensively used as a plating upon other metals, such as iron or brass, to prevent tarnishing in air, and cobalt can be used in the same way. Finely divided nickel is used as a catalyzer in a number of reactions, such as the conversion of oils into solid fats (p. 343) and in the oxidation of ammonia into nitric acid.

FIG. 192. The process of electroplating with nickel

Electroplating with nickel. Nickel plating is accomplished by an electrolytic process. The electrolyte consists of a solution of nickel ammonium sulfate, a salt having the composition

$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$. The object to be plated is suspended in the electrolyte and serves as the cathode, while a plate of nickel is used as the anode. When the current is passing through the electrolyte, the nickel is deposited upon the object to be plated, and an equivalent portion of nickel dissolves from the anode, the composition of the electrolyte remaining unchanged. Fig. 192 illustrates the process carried out on a large scale, the objects to be plated being suspended from the rods *A*, *A*.

Cobalt oxide (CoO). This is the form in which most of the cobalt comes into the market. It is a black powder used in making other cobalt compounds and in making blue glass and blue decorations on china. Sometimes ground blue cobalt glass, called *smalt*, is used instead of the oxide and as a pigment.

Salts of cobalt and nickel. Nearly all the simple salts of cobalt and of nickel have formulas similar to those of *ferrous* salts. The most familiar are the following:

$Co(NO_3)_2 \cdot 6\ H_2O$	a cherry-red deliquescent salt
$CoCl_2 \cdot 6\ H_2O$	similar in appearance to the nitrate
CoS	an insoluble black precipitate
$NiSO_4 \cdot 7\ H_2O$	well-formed green crystals
$Ni(NO_3)_2 \cdot 6\ H_2O$	deliquescent green crystals
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$.	used in nickel plating
NiS	an insoluble black precipitate

EXERCISES

1. In the manufacture of cast iron, why is the air heated before being forced into the furnace?

2. Write the equations showing how each of the following compounds of iron could be obtained from the metal itself: ferrous chloride, ferrous hydroxide, ferrous sulfate, ferrous sulfide, ferrous carbonate, ferric chloride, ferric sulfate, ferric hydroxide.

3. Account for the fact that a solution of sodium carbonate when added to a solution of a ferric salt precipitates a hydroxide and not a carbonate.

4. Calculate the percentage of iron in each of the common iron ores.

5. Why is brass often nickel plated?

6. Why does not iron occur in the native state? What does its native occurrence in meteorites indicate?

7. Why is the furnace in which cast iron is made called a blast furnace?

8. Write equations for the oxidation of ferrous sulfate to ferric sulfate; for the reduction of ferric sulfate to ferrous sulfate.

9. Suggest a method for removing the iron from chalybeate waters.

10. Why is the formula for Prussian blue written $Fe_4(FeC_6N_6)_3$ rather than $Fe_7(C_6N_6)_3$?

11. Will ammonium hydroxide precipitate ferric hydroxide when added to a solution of sodium ferrocyanide?

12. What weight of iron disulfide is necessary for the preparation of 1000 kg. of 50 per cent of sulfuric acid?

13. One ton of steel prepared by the Bessemer process is found by analysis to contain 0.2 per cent of carbon. What is the minimum weight of carbon which must be added in order that the steel may be made to take a temper?

CHAPTER XXXIX

COPPER, MERCURY, AND SILVER

Name	Symbol	Atomic weight	Density	Melting point	Formulas of oxides	
					-ous	*-ic*
Copper . . .	Cu	63.57	8.93	1083.0°	Cu_2O	CuO
Mercury . . .	Hg	200.60	13.56	– 38.9°	Hg_2O	HgO
Silver	Ag	107.88	10.50	960.5°	Ag_2O	AgO

The family. Although mercury is not in the same family with copper and silver, the three elements resemble each other so closely in chemical conduct that it is convenient to class them together for study. Gold belongs in this family, but will be described later.

Occurrence and properties. The three elements occur in nature to some extent in the free state, but are usually found as sulfides. Their oxides are easy to reduce.

All three are heavy metals of high luster and are especially good conductors of heat and electricity. They are not very active chemically. They occur below hydrogen in the displacement series, and as a consequence neither hydrochloric nor dilute sulfuric acid has any appreciable action upon them. Concentrated sulfuric acid attacks all three, forming metallic sulfates and evolving sulfur dioxide (p. 247), while nitric acid, both dilute and concentrated, converts them into nitrates with the evolution of oxides of nitrogen (p. 210).

Two series of salts. Copper and mercury form oxides of the types M_2O and MO, as well as two series of salts. In one series the metals are univalent and the salts have formulas like those of the sodium salts. They are called cuprous and mercurous salts. In the other series the metals are bivalent and resemble magnesium salts in formulas. These are called cupric and mercuric salts. Silver forms only one series of salts, being always a univalent metal.

Fig. 193. Mining copper ore at Butte, Montana

Copper

Occurrence. The element copper has been used for various purposes since the earliest days of history. It is often found in the native state, large masses of it occurring nearly pure in the Lake Superior region and, to a smaller extent, in other places. Apart from native copper the most valuable ores are the following:

SULFUR ORES		OXYGEN ORES	
Chalcopyrite . . .	$CuFeS_2$	Cuprite . .	Cu_2O
Chalcocite	Cu_2S	Melaconite .	CuO
Bornite	Cu_5FeS_4	Malachite .	$CuCO_3 \cdot Cu(OH)_2$

Metallurgy of copper. Ores containing little or no sulfur are easy to reduce. They are first crushed and the earthy impurities washed away. The concentrated ore is then mixed with carbon and a flux and heated in a furnace, metallic copper resulting from the reduction of the copper oxide by the hot carbon.

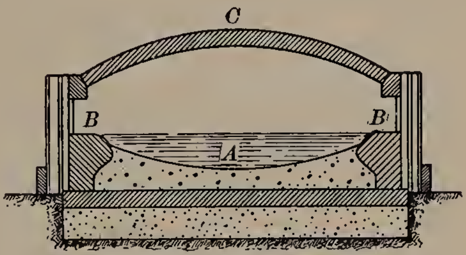


Fig. 194. Vertical section of a reverberatory furnace

Metallurgy of sulfur ores. Much of the copper of commerce is made from chalcopyrite and bornite, and these ores are more difficult to work, partly because they are sulfides and cannot be reduced by heating with carbon, and partly because they contain a great deal of iron as well as copper.

If the ore is in fine grains it is first smelted in a *reverberatory furnace* (Fig. 194). This is a long and rather narrow furnace with a concave floor (*A*) on which the ore *B*, together with silicious flux, is placed through a row of openings along the sides of the roof. The ore is heated by a long flame from burning coal led through the furnace, the heat from the flame being reflected down upon the charge from the arched roof *C*. Sometimes the flame is maintained by blowing powdered coal through the furnace.

A part of the sulfur is burned and a part of the iron is converted into iron oxide, which then combines with the silica to make a slag of ferrous silicate. The copper sulfide, together with the remaining iron sulfide, melts to form a heavy liquid called *matte*, which collects under the slag.

If the ore is coarse, so that an air blast will not blow it away, the matte is made in a blast furnace resembling the one used for making cast iron, only much smaller.

The liquid matte is then tapped off into a *converter* closely resembling the one used in the Bessemer process and holding sometimes as much as 50 tons. Some silica is added and a carefully regulated current of air is blown in. The sulfur acts as fuel, burning to form sulfur dioxide; the iron is converted into oxide, which then combines with the silica to form slag; the copper sulfide burns to form sulfur dioxide and copper. When the process is complete the liquid copper is drawn off and poured into molds. It is called *blister* copper and may be as high as 98 per cent pure. The United States produces an enormous tonnage of copper annually.

Refining of copper. Blister copper is purified by electrolysis. A large plate of it, serving as an anode, is suspended in a tank, facing a thin plate of pure copper which is the cathode. The tank is filled with a solution of copper sulfate and sulfuric acid to act as the electrolyte. A current from a dynamo passes from the anode to the cathode, and the copper, dissolving from the anode, is deposited upon the cathode in pure form, while the impurities collect on the bottom of the tank. Electrolytic copper is one of the purest of commercial metals.

Recovery of gold and silver. Gold, silver, and nickel are often present in small quantities in copper ores, and remain in the crude copper. In electrolytic refining the gold and silver collect in the muddy deposit on the bottom of the tank. The mud is carefully worked over from time to time and the precious metals extracted from it. A surprising amount of gold and silver is obtained in this way. The nickel passes into solution and is recovered from the electrolyte (p. 489).

Properties of copper. Copper is a rather heavy metal, of density 8.9, and has a characteristic reddish color. It is rather soft and is very malleable, ductile, and flexible, yet tough and strong; it melts at 1083° and boils at 2310°. As a conductor of heat and electrical energy it is second only to silver.

Since it is below hydrogen in the displacement series, hydrochloric acid, dilute sulfuric acid, and fused alkalies are almost without action upon it; nitric acid and hot concentrated sulfuric acid, however, readily dissolve it (pp. 210, 247). In moist air it slowly becomes covered with a film of the bright-red oxide Cu_2O, which soon changes to a green basic carbonate. If heated in the air the metal is easily oxidized to the black oxide CuO.

Uses. Copper is extensively used for electrical purposes, for roofs and cornices, for sheathing the bottoms of ships, and for making alloys. In the following table the composition of some of these alloys is indicated:

Aluminium bronze . .	90%–98% copper, 2%–10% aluminium
Brass	63%–73% copper, 27%–37% zinc
Bronze	70%–95% copper, 1%–25% zinc, 1%–18% tin
German silver . . .	50%–60% copper, 20% zinc, 20%–30% nickel
Gun metal	90% copper, 10% tin
Gold coin	10% copper, 90% gold
Silver coin	10% copper, 90% silver
Nickel coin	75% copper, 25% nickel

Electrotyping. Books are often printed from electrotype plates, which are prepared as follows: The face of the type is covered with wax, and this is firmly pressed down until a clear impression is obtained. The impressed side of the wax is coated with graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

Two series of copper compounds. Copper, like iron, forms *two series* of compounds: the *cuprous* compounds, in which it is univalent; and the *cupric* compounds, in which it is bivalent. The cupric salts are much the more common of the two.

Cuprous compounds. The most important cuprous compound is the oxide, Cu_2O, which occurs in nature as *ruby copper*, or *cuprite*. It is a bright-red substance and can easily be prepared by heating copper to a high temperature in a limited supply of air. It is used for imparting a ruby color to glass. By treating cuprous oxide with different acids a number of cuprous salts can be made.

Cuprous chloride (CuCl) is the best-known cuprous salt. It can be made by boiling a solution of cupric chloride with copper:

$$CuCl_2 + Cu \longrightarrow 2\,CuCl$$

It is a white salt, nearly insoluble in water.

Cupric compounds. Cupric salts are easily made by dissolving cupric oxide in acids or, when insoluble, by precipitation. In crystallized form most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are frequently called merely copper salts.

Cupric oxide (CuO). This is a black insoluble substance obtained by heating copper in excess of air or by igniting the hydroxide or the nitrate. It is used as an oxidizing agent.

Cupric sulfate ($CuSO_4$). When crystallized from water, cupric sulfate forms large blue crystals of the hydrate

$CuSO_4 \cdot 5\,H_2O$, called *blue vitriol*, or *bluestone*. The salt is a by-product in silver refining, and is also made by the oxidation of pyrite containing copper:

$$CuS + 2\,O_2 \longrightarrow CuSO_4$$

The salt finds extensive use in electrotyping, in copper refining, as a remedy for hoof diseases (particularly in sheep), and in the manufacture of insecticides. Like all copper salts, it is poisonous, especially to lower forms of life. When added even in very minute quantities to water containing green pond scum (algæ), the plant is quickly killed. Mixed with milk of lime (which precipitates copper hydroxide) it constitutes *Bordeaux mixture*, which is used as a spray for killing molds and scale on fruit trees and vegetables.

Cupric sulfide (CuS). In the form of a black insoluble precipitate, cupric sulfide (CuS) is easily prepared by the action of hydrogen sulfide upon a solution of a copper salt:

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

It is insoluble in water and in dilute acids.

Other cupric salts. Among the other cupric salts frequently used in the laboratory are the following, most of which form other hydrates in addition to those given:

Cupric nitrate ($Cu(NO_3)_2 \cdot 6\,H_2O$): blue deliquescent crystals
Cupric chloride ($CuCl_2 \cdot 2\,H_2O$): light-blue pearly scales or needles
Cupric bromide ($CuBr_2$): brownish-purple crystals resembling iodine
Cupric acetate ($Cu(C_2H_3O_2)_2 \cdot H_2O$): a blue, easily crystallized salt

Cupric ammonia compounds. When cupric sulfate in solution is treated with aqua ammonia the insoluble hydroxide is at first precipitated:

$$CuSO_4 + 2\,NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

Continued addition of ammonia causes the precipitate to dissolve, forming an intensely colored blue-purple solution. By adding alcohol to the solution a colored salt crystallizes, which is found to have the formula $Cu(NH_3)_4SO_4 \cdot H_2O$. In solution this salt does not give simple cupric ions (Cu^{++}), but the cation is $Cu(NH_3)_4^{++}$ and the anion is SO_4^{--}. All soluble copper salts give a solution of this same blue-purple color when treated with an excess of ammonia, and all of these solutions contain the complex cation $Cu(NH_3)_4^{++}$. The anion may be any acid radical, so that we have such salts as the following: $Cu(NH_3)_4Cl_2$; $Cu(NH_3)_4(NO_3)_2$; $Cu(NH_3)_4CO_3$. Many other metals form similar salts, especially cobalt, nickel, and platinum, and these are sometimes called *ammine salts.*

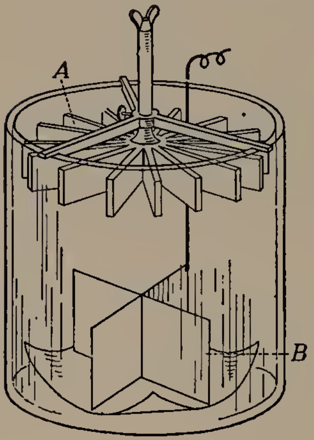


FIG. 195. A simple type of electric cell, called the Daniell cell

Electric cells. An electric cell is a device for converting chemical energy directly into electrical energy. A great many different chemical reactions can be arranged in such a way as to accomplish this result, and the combination known as the Daniell cell will serve as an illustration of the most familiar types of cells. In this combination two plates, one of copper and the other of zinc, each fashioned so as to have a large surface, are arranged in a glass jar, as shown in Fig. 195. The electrolyte in contact with the zinc plate is zinc sulfate, while that in contact with the copper plate is copper sulfate.

The action of the cell can be explained as follows: The zinc atoms of the plate *A* have a tendency to leave the plate and to pass into solution as zinc ions. But since each zinc ion (Zn^{++}) carries two positive charges, the formation of these ions leaves the plate negatively charged. The accumulation of this charge soon prevents the formation of more zinc ions and the process stops in an equilibrium.

On the other hand, copper ions (Cu^{++}) from the dissolved copper sulfate have a tendency to deposit upon the copper plate *B* as metallic atoms, each copper ion bringing to the plate two positive charges. The accumulation of these charges on the plate soon prevents the deposit of more copper ions, and equilibrium results.

If now the two plates are joined by an electrical conductor (a metal wire) the negative charge on the zinc plate neutralizes the positive charge on the copper plate by flowing through the wire. The solution of the zinc and the deposit of the copper can now proceed as long as the two plates are connected. The chemical reaction taking place is represented by the equation:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu + 50{,}100 \text{ cal.}$$

In this particular reaction nearly all of the heat is converted into electrical energy, which may be obtained from the wire and may be in turn converted into light or work.

The order of the metals in the electromotive series (p. 191) is the order of intensity with which the metals tend to pass into ionic form. Any two metals in a suitable electrolyte will constitute a cell in which the metal higher in the series is the negative pole and the lower one the positive. As a rule, only a part of the chemical energy is converted into electrical energy, the remainder being transformed into heat.

MERCURY

Occurrence. Mercury occurs in nature chiefly as the sulfide HgS, called *cinnabar.* The mercury mines of Spain have long been famous, and California is the next largest producer.

Metallurgy. Mercury is a volatile metal which has but little affinity for oxygen, and this makes the metallurgy of mercury very simple. The crushed ore, mixed with a small amount of carbon to reduce any oxide or sulfate that might be formed, is roasted in a current of air. The sulfur burns to sulfur dioxide, while the mercury vaporizes and is condensed in a series of condensing vessels. The metal is purified by distillation.

Properties. Mercury is a heavy, silvery liquid, with a density of 13.56. It boils at 357° and solidifies at $-38.9°$. It forms alloys (called amalgams) with nearly all metals.

Toward acids mercury conducts itself very much like copper; it is easily attacked by nitric acid and by hot concentrated sulfuric acid, while cold sulfuric acid and hydrochloric acid have no effect on it.

Uses. Mercury is extensively used in the construction of many scientific instruments, such as the thermometer and the barometer, and as a liquid over which to collect gases that are soluble in water. The readiness with which it alloys with silver and gold makes it very useful in the extraction of these elements. All salts of mercury are made directly or indirectly from the purified metal.

Compounds of mercury. Like copper, mercury forms two series of compounds: the *mercurous* compounds, of which mercurous chloride ($HgCl$) is an example; and the *mercuric* compounds, represented by mercuric chloride ($HgCl_2$).

Mercuric oxide (HgO). Mercuric oxide is usually obtained as a brick-red substance by carefully heating the nitrate:

$$2\,Hg(NO_3)_2 \longrightarrow 2\,HgO + 4\,NO_2 + O_2$$

It can also be obtained in a yellow form. When heated, the oxide darkens until it becomes almost black; at a higher temperature it decomposes into mercury and oxygen (p. 25).

Mercuric sulfate ($HgSO_4$). This salt is easily prepared by the action of an excess of concentrated sulfuric acid upon mercury, the reaction being like that of sulfuric acid upon copper (p. 247). It is a white solid, soluble in dilute sulfuric acid, but hydrolyzed into a yellow basic salt by pure water. It is the cheapest salt of mercury.

Mercuric chloride (corrosive sublimate) ($HgCl_2$). This substance can be made by dissolving mercuric oxide in hydrochloric acid. On a commercial scale it is made by heating a mixture of common salt and mercuric sulfate:

$$2\,NaCl + HgSO_4 \longrightarrow HgCl_2 + Na_2SO_4$$

The mercuric chloride, being readily volatile, vaporizes and is condensed again in cool vessels. It is a white solid and is soluble in water. It is extremely poisonous and in dilute solutions is used as an antiseptic in dressing wounds.

Mercurous chloride (calomel) ($HgCl$). Being insoluble, mercurous chloride is precipitated as a white solid when a soluble chloride is added to a solution of mercurous nitrate:

$$HgNO_3 + NaCl \longrightarrow HgCl + NaNO_3$$

Commercially it is manufactured by heating a mixture of mercuric chloride and mercury. It is a common medicine.

Mercuric sulfide (HgS). As cinnabar, this substance forms the chief native compound of mercury, and occurs in red crystalline masses. By passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is precipitated as a *black* powder insoluble in water and acids. By other means it can be prepared as a brilliant red powder, known as *vermilion*, which is used as a pigment in fine paints.

Other salts of mercury. The following salts have frequent uses in the laboratory:

Mercurous nitrate ($HgNO_3 \cdot 2\,H_2O$): colorless crystals soluble in dilute nitric acid

Mercuric nitrate, $Hg(NO_3)_2 \cdot 8\,H_2O$: colorless crystals soluble in dilute nitric acid

Mercurous sulfate (Hg_2SO_4): white crystalline solid nearly insoluble in dilute acids

Mercuric fulminate, $Hg(ONC)_2$: a white solid made by the action of nitric acid upon mercury in the presence of alcohol. It is used as the explosive material in percussion primers

SILVER

Occurrence. Silver is found in small quantities in the uncombined state; usually, however, it occurs in combination with sulfur, either as the sulfide Ag_2S or as a constituent of other sulfides, especially those of lead, copper, antimony, and arsenic. It is also found alloyed with gold.

In this country silver is produced almost entirely in connection with lead, and it will be convenient to consider the metallurgy of the two metals together in the next chapter.

The United States produces about one third of the world's output of silver, and America, including Mexico and Canada, about 70 per cent.

The refining of silver. Crude silver obtained by any process may contain a number of metals, especially copper and gold, and is usually refined either by *parting* with sulfuric acid or by electrolysis.

1. ***Cupellation and parting with sulfuric acid.*** In this process the impure metal is heated on an open hearth in a strong current of air. The various metallic impurities

(excepting gold) are in this way largely converted into oxides and swept off as dross, leaving the silver alloyed with small percentages of gold, copper, and iron. It is then cast into ingots known as *doré* bars, since they contain gold.

In order to recover the gold the alloy is treated with hot concentrated sulfuric acid, which converts into sulfates all the metals except the gold. When water is added to the resulting mixture the sulfates of copper, silver, and iron pass into solution, while the gold, together with the lead sulfate and any unattacked substances, settles as a mud from which the gold is subsequently recovered. The silver is separated from the solution of the sulfates by suspending in the latter clean copper plates, the copper displacing the silver, which is deposited in crystalline form:

$$Ag_2SO_4 + Cu \longrightarrow CuSO_4 + 2\,Ag$$

The copper sulfate obtained as a by-product in this process furnishes much of the blue vitriol of commerce.

2. ***Electrolytic refining.*** Electrolysis of the impure silver is now carried out extensively, the process being conducted in a way very similar to the electrolysis of copper. The electrolyte used is a solution of silver nitrate in nitric acid. The silver is deposited as crystals, which are mechanically brushed off the cathode, collected, and melted into bars.

Properties of silver. Silver is a heavy, rather soft, white metal, very ductile and malleable, and capable of taking a high polish. It surpasses all other metals as a conductor of heat and electricity, but is too costly to find extensive use for such purposes. It melts at a little lower temperature than copper. It alloys readily with other heavy metals, and when it is to be used for coinage or for tableware, a small amount of copper — from 8 per cent to 10 per cent — is melted with it to give it hardness (sterling silver).

It is not acted upon by water or air, but is quickly tarnished when in contact with sulfur compounds (eggs, mustard, perspiration), turning quite black in time. Hydrochloric acid and fused alkalies do not act upon it, but nitric acid and hot concentrated sulfuric acid dissolve it with ease. When a solution of a silver salt is treated with a strong reducing agent, metallic silver is precipitated. Under proper conditions this takes the form of a brilliant mirror deposited on the sides of the glass vessel. *Mirrors* and glass reflectors are usually made in this way.

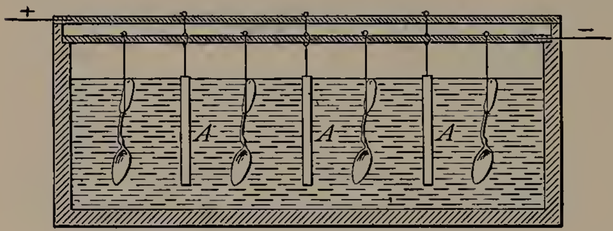


FIG. 196. The process of silver plating

Electroplating with silver. Since silver is not acted upon by water or air and has a pleasing appearance, it is used to coat various articles made of cheaper metals. Such articles are said to be *silver plated,* and the process by which this is done is very similar to electroplating with nickel (p. 490). The object to be plated (as, for example, a spoon) is attached to a wire and dipped into a solution of a suitable silver salt. Electrical connection is made in such a way that the article to be plated is the cathode (Fig. 196), while the anode *A* is made up of one or more plates of silver.

Compounds of silver. Silver forms only one series of salts, which corresponds to the mercurous and the cuprous series.

Silver nitrate (lunar caustic) ($AgNO_3$). This salt is easily prepared by dissolving silver in nitric acid and evaporating the resulting solution. It crystallizes in flat, colorless plates, and when heated carefully can be melted without decomposition. When cast into sticks it is called *lunar caustic*, for it has a very corrosive action on flesh and is sometimes used in surgery to burn away abnormal growths.

The alchemists designated the metals by the names of the heavenly bodies. The moon (*luna*) was the symbol for silver; hence the name *lunar caustic.*

Some less important salts. The following is a list of some of the silver salts used in the arts or in analysis:

Silver sulfate (Ag_2SO_4): a sparingly soluble salt crystallizing in white needles
Silver nitrite ($AgNO_2$): a white salt soluble in hot water
Silver sulfide (Ag_2S): found in nature as *argentite.* It is insoluble both in water and in acids and may be prepared by precipitation as a black powder
Silver cyanide ($AgCN$): a curdy white precipitate insoluble in water
Silver chromate (Ag_2CrO_4): a brick-red solid prepared by precipitation

Compounds of silver with the halogens. The chloride ($AgCl$), the bromide ($AgBr$), and the iodide (AgI) are insoluble in water and in acids and therefore are precipitated by bringing together a soluble halogen salt with silver nitrate:

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

These salts are remarkable for the fact that they are very sensitive to the action of light, undergoing a change of color and chemical composition when exposed to sunlight. It is thought that this change consists in a partial decomposition according to the equilibrium equation:

$$AgCl \rightleftarrows Ag + Cl$$

If some material is present that will absorb chlorine, such as gelatin, the action is more pronounced. In this case the gelatin is called a *sensitizer*. It is upon these general facts that the art of photography is based.

Fig. 197. The negative plate

Photography. From a chemical standpoint the processes of photography may be described under two heads: (1) the preparation of the negative; (2) the preparation of the print.

1. ***Preparation of the negative.*** The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is sometimes added also), over a glass plate or celluloid film and allowing it to dry. When the plate so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a change which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is therefore called latent. It can be made visible by the process of *developing*.

Fig. 198. The positive print

To develop the image the exposed plate is immersed in a solution of some reducing agent called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is deposited in the form of a black film which adheres closely to the plate.

The unaffected silver salt is now removed from the plate by immersing it in a solution of sodium thiosulfate (*hypo*). The plate is then washed with water and dried. The plate so prepared is called the *negative* (Fig. 197), because it is a picture of the object photographed, with the lights and positions exactly reversed.

2. *Preparation of the print.* The print is made on paper which is prepared in much the same way as the negative plate. The negative is placed upon this paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride, a visible image is produced, in which case a developer is not needed. *Proofs* are made in this way. In order to make them permanent the unchanged silver chloride must be dissolved off with sodium thiosulfate. The print is then *toned* by dipping it into a solution of gold or platinum salts, in which process the silver on the print passes into solution, while the gold or platinum takes its place. These metals give a characteristic color or tone to the print, the gold making it reddish brown, while the platinum gives it a steel-gray tone. Since the darkest places on the negative cut off the most light, it is evident that the lights of the print (Fig. 198) will be the reverse of those of the negative, and will therefore correspond to those of the object photographed.

EXERCISES

1. Why has copper or bronze been used for so long a time?

2. Why do we have so many relics from the bronze age and so few from the iron age?

3. Why is a solution of copper sulfate acid to litmus paper?

4. How should you account for the fact that so many different salts of copper have the same blue color in dilute solutions?

5. How could you distinguish between mercurous chloride and mercuric chloride?

6. Crude silver usually contains iron and lead. What would become of these in refining silver by *parting* with sulfuric acid?

7. Mercuric nitrate and silver nitrate are both white soluble solids. How could you distinguish between them?

8. How do you account for the fact that a silver spoon gradually darkens when in contact with eggs?

9. Why are copper, mercury, and silver all found to some extent native in nature?

10. What properties make mercury useful in thermometers and in barometers?

11. Write equations for the action of concentrated sulfuric acid on mercury; of nitric acid on silver.

12. Suggest a method for obtaining pure silver from a silver coin.

13. When a solution of silver nitrate is added to a solution of potassium chlorate, no precipitate forms. How do you account for the fact that a precipitate of silver chloride is not formed?

14. Which of the ores of copper contains the largest percentage of copper?

15. What would be the effect of immersing an unexposed photographic film in a solution of sodium thiosulfate?

16. One ton of cinnabar will yield how many pounds of mercury?

17. Suppose you wish to prepare 1000 g. of calomel, what substances and what weight of each would be required?

18. A silver dollar weighs approximately 26.5 g. What weight of silver nitrate could be prepared from such a coin?

CHAPTER XL

TIN AND LEAD

Name	Symbol	Atomic weight	Density	Melting point	Common oxides
Tin	Sn	118.7	7.3	231.9°	SnO SnO_2
Lead . . .	Pb	207.20	11.37	327.4°	PbO Pb_3O_4 PbO_2

Tin

Occurrence. Tin is found in nature chiefly as the oxide SnO_2, called *cassiterite*, or *tinstone*. The most famous mines are in Cornwall, in the East Indies, and in Bolivia. Very little is produced in the United States from domestic ores.

Metallurgy. In principle the metallurgy of tin is very simple. The ore, separated as far as possible from earthy materials, is mixed with carbon and heated in a furnace, the reduction taking place readily. The equation is

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The chief difficulty is in freeing the tin from iron, and commercial tin often contains a considerable percentage of the latter element. The metal is often purified by carefully heating it until it is partly melted; the pure tin melts first and can be drained away from the impurities.

Properties. Pure tin, called *block* tin, is a soft white metal with a silverlike appearance and luster; it melts readily and is somewhat lighter than copper, having a density of 7.3. It is malleable and can be rolled out into very thin sheets, forming *tin foil*; most tin foil, however, contains a considerable percentage of lead.

Under ordinary conditions tin is unchanged by air or moisture, but at a high temperature it burns, forming the oxide SnO_2. Dilute acids have little effect upon it, but concentrated acids attack it readily. Concentrated hydrochloric acid changes it into the chloride:

$$Sn + 2\,HCl \longrightarrow SnCl_2 + H_2$$

With sulfuric acid, stannous sulfate and sulfur dioxide are formed:

$$Sn + 2\,H_2SO_4 \longrightarrow SnSO_4 + SO_2 + 2\,H_2O$$

Concentrated nitric acid oxidizes it, forming a white insoluble compound, H_2SnO_3, called *metastannic acid.*

Uses of tin. A great deal of tin is used in the making of *tin plate.* The process consists in dipping thin sheets of iron into the melted tin and is quite similar to that of galvanizing iron (p. 447). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, such as in roofing and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin (p. 497). *Pewter* and *soft solder* are alloys of tin and lead.

Rusting of tin plate. If the coating of tin on tin plate is scratched through to the iron, the iron will rust faster than if there were no tin covering. The two metals and the water constitute a battery, much like the Daniell cell (p. 500), and in a battery the metal highest in the displacement series is the one that is corroded. In the case of galvanized iron the zinc rusts first, and the iron resists rusting as long as any zinc is present.

Soldering and brazing. The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable flux must be used which will either *dissolve* the oxide as fast as it forms or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing*, or *hard soldering*, the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

Compounds of tin. Tin forms two series of compounds: the stannous, in which the tin is bivalent, illustrated in the compounds SnO, SnS, $SnCl_2$; the stannic, in which it is tetravalent, as shown in the compounds SnO_2, SnS_2. There is also an acid, H_2SnO_3, called stannic acid, which forms a series of salts called stannates. Only a few compounds of tin need be described.

Stannic oxide (SnO_2). Stannic oxide is of interest, since it is the chief compound of tin found in nature. It is sometimes found in good-sized crystals, but as prepared in the laboratory it is a white powder. When stannic oxide is fused with potassium hydroxide it forms potassium stannate, acting very much like silicon dioxide:

$$SnO_2 + 2\,KOH \longrightarrow K_2SnO_3 + H_2O$$

Stannic acid (H_2SnO_3). The compound H_2SnO_3 can be prepared in a number of ways, and it is a white solid, insoluble in water. It is a remarkable fact that its chemical properties depend to a large extent upon the way in which it is made. Some methods yield a product that is readily soluble in dilute acids, while the product formed by the action of concentrated nitric acid upon tin is insoluble in acids and is called *metastannic acid.* The soluble forms are colloidal in character, and it is probable that the differences in the precipitated colloids are due to the size of the particles formed rather than to a different chemical structure of the compounds.

Chlorides of tin. Stannous chloride is prepared by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. The crystals which are obtained have the composition $SnCl_2 \cdot 2\,H_2O$ and are known as *tin crystals.* By treating a solution of stannous chloride with aqua regia, stannic chloride is formed:

$$SnCl_2 + 2\,[Cl] \longrightarrow SnCl_4$$

The salt which crystallizes from such a solution has the composition $SnCl_4 \cdot 5\,H_2O$ and is known commercially as *oxymuriate of tin.* If metallic tin is heated in a current of dry chlorine, the anhydrous chloride ($SnCl_4$) is obtained as a heavy colorless liquid which fumes strongly on exposure to air. A great deal of stannic chloride is recovered from scrap tin plate by *detinning* with chlorine.

The ease with which stannous chloride takes up chlorine to form stannic chloride makes it a good reducing agent in many reactions, changing the higher chlorides of metals to lower ones. Thus mercuric chloride is changed into mercurous chloride:

$$SnCl_2 + 2\,HgCl_2 \longrightarrow SnCl_4 + 2\,HgCl$$

If the stannous chloride is in excess the reaction may go further, producing metallic mercury:

$$SnCl_2 + 2\,HgCl \longrightarrow SnCl_4 + 2\,Hg$$

Ferric chloride is in like manner reduced to ferrous chloride:

$$SnCl_2 + 2\,FeCl_3 \longrightarrow SnCl_4 + 2\,FeCl_2$$

The chlorides of tin, as well as the alkali stannates, are much used as mordants in dyeing processes. The hydroxides of tin and free stannic acid, which are easily liberated from these compounds, possess in very marked degree the power of fixing dyes upon fibers, as explained under aluminium (p. 458).

Other compounds of tin. A few of the other important compounds are included in the following list:

Stannous sulfide (SnS): a nearly black precipitate formed by the action of hydrogen sulfide upon a stannous salt
Stannic sulfide (SnS_2): a bright-yellow precipitate formed by the action of hydrogen sulfide upon a stannic salt
Ammonium chlorostannate, $(NH_4)_2SnCl_6$: a well-crystallized salt used as a mordant in dyeing, and called *pink salt*

LEAD

Occurrence. Lead is found in nature chiefly as the sulfide PbS, called *galenite.* In the United States this is mined principally in Missouri (Fig. 199) and Idaho.

Metallurgy of lead. Almost all the lead of commerce is made from galenite, which usually contains some silver To obtain this silver most economically it is customary to combine richer silver ores with lead ores and work the two together.

Reduction of silver-bearing lead ores. The sulfide ores are first roasted until a part of the sulfide has been changed into the oxide and the sulfate. The air is then shut off and the heating continued, which brings about the reactions indicated in the following equations:

$$2\,PbO + PbS \longrightarrow 3\,Pb + SO_2$$
$$PbSO_4 + PbS \longrightarrow 2\,Pb + 2\,SO_2$$

By reactions which are similar to the above the silver compounds are reduced, the silver alloying with the lead. In some more recent plants the ores are roasted until nearly all of the sulfide has been oxidized. The roasted ore is then mixed with coke and heated in a furnace like a copper matte furnace. All lead oxide is reduced to lead, while the lead sulfate is reduced to lead sulfide and forms a liquid matte. This is drawn off and once more roasted.

The softening of lead. The lead obtained in this way is called *hard* lead, and in addition to silver contains smaller quantities of other elements, especially of copper, arsenic, antimony, gold, and bismuth. The lead is *softened* by melting it in an open furnace with free access of air. This converts most of the impurities (as well as some lead) into oxides which float upon the melted lead and can easily be removed. The partially purified lead is called *soft* lead.

FIG. 199. Mining galenite in the Joplin region in Missouri

Desilverizing of lead (the Parkes process). The lead is melted in large kettles holding as much as 30 tons, and about 1 per cent of zinc is stirred in. These two metals do not mix to any great extent, and gold, silver, and copper are much more soluble in zinc than in lead. Consequently when the stirring ceases, the zinc rises to the surface of the lead, carrying with it the other metals. The zinc is then skimmed off and distilled (by which process the zinc is recovered to be used again), and the residue of silver and gold is melted down and cast into ingots called *doré* bars. These are refined as explained under silver (p. 505). An electrolytic method (*Betts process*) is now being used similar to the one employed with copper, but with many special details.

Properties. Lead is a heavy metal which has a brilliant silvery luster on a freshly cut surface, but which soon tarnishes by oxidation to a dull blue-gray color. It is soft, easily fused (melting at 327.4°), and malleable, but has little toughness or strength.

It is not acted upon to any great extent, under ordinary conditions, by the oxygen of the air, but at a high temperature is changed into the oxide. With the exception of hydrochloric and sulfuric acids (which form insoluble compounds), most acids, even very weak ones, act upon it, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it to a slight extent.

Uses. Lead finds many important applications in the industries, chiefly in the manufacture of storage batteries, in linings for sulfuric acid plants, in alloys of various kinds (such as shot, antifriction metals, type metal, and pewter), and in water pipes for plumbing. Since lead dissolves to some extent in pure water, it should not be used for pipes that are to carry rain water. About one third of the annual production of lead is used in making paint, and is permanently lost.

Compounds of lead. In nearly all its compounds lead is bivalent, but in a few of its compounds it has a valence of four. All of its compounds are poisonous.

Lead oxides. Lead forms a number of oxides, the most important of which are the following:

1. *Litharge, massicot* (*PbO*). This oxide forms when hot lead is oxidized by the air. If the temperature is high enough to melt the oxide, the color of the product is deep yellow or even red, and the oxide is called *litharge*. It is used in the preparation of boiled linseed oil and in glassmaking. If the oxide is not melted, it forms a light yellow powder called *massicot*, which is used in making red lead.

2. *Red lead, or minium* (Pb_3O_4). Minium is prepared by heating lead (or massicot) to a high temperature in contact with a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron. Mixed with linseed oil it forms a cement used in joining gas pipes.

3. *Lead peroxide* (PbO_2). This is left as a residue when minium is heated with nitric acid:

$$Pb_3O_4 + 4\,HNO_3 \longrightarrow 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O$$

It is a brown powder which easily gives up a part of its oxygen and, like manganese dioxide and barium dioxide, is a good oxidizing agent.

Lead sulfide (PbS). In nature this compound occurs in a highly crystalline form called *galenite*, the crystals having much the same color and luster as pure lead. It is readily prepared in the laboratory as a black precipitate, by the action of hydrogen sulfide upon soluble lead salts:

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS + 2\,HNO_3$$

It is insoluble both in water and in dilute acids.

Lead carbonate. While the normal carbonate of lead, $PbCO_3$, is found to some extent in nature and can be prepared in the laboratory, basic carbonates of varying composition are much more easy to obtain. One of the simplest of these has the composition $2\,PbCO_3 \cdot Pb(OH)_2$ and is called *white lead.* This is prepared on a large scale as a white pigment and as a body for paints which are to be colored with other substances.

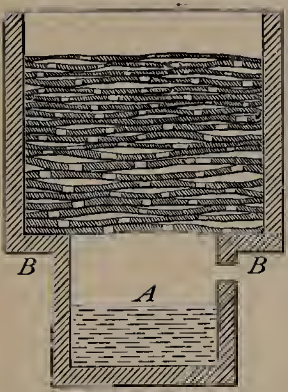


FIG. 200. A crock filled with thin lead plates for making white lead

Manufacture of white lead. White lead can be prepared by a number of processes, but no other seems to produce a product of as desirable physical properties as the old Dutch process, which has been used for centuries, though with many improvements. In this process the lead is cast into perforated plates called *buckles*, which are placed loosely upon each other in a crock of the shape shown in Fig. 200, the ledge *B*, formed by the constriction of the crock, supporting the plates. Under them in *A* is poured a suitable quantity of dilute acetic acid, and the crocks so charged are placed in banks and covered with stable manure or spent tanbark. The heat of fermentation in the latter warms the acid, the fumes of which attack the lead, forming lead acetate. The carbon dioxide from the fermentation enters into reaction with the acetate, producing the basic carbonate and regenerating acetic acid. This acid acts again upon the lead, and the process continues until the buckles are almost completely converted into the desired compound. Fig. 201 shows a buckle before and after the corrosion, the white carbonate resembling enamel.

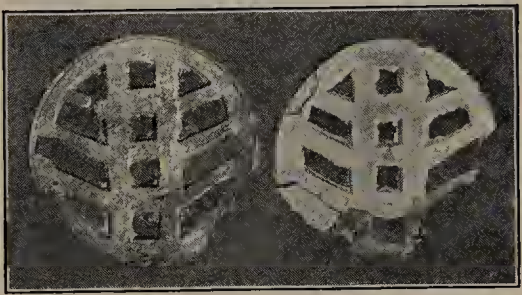


FIG. 201. Lead buckles before and after exposure to acetic acid and carbon dioxide

A more modern process, known as Carter's process, is much used. Very finely powdered lead is placed in a rotating barrel, and dilute acetic acid is sprayed in. Carbon dioxide is admitted at the same time, and the process is continued for about two weeks.

Other important compounds of lead. Soluble salts of lead are obtained by dissolving litharge in the appropriate acid. Insoluble salts are obtained by precipitation. Some of the most important are the following:

Lead nitrate, $Pb(NO_3)_2$: white soluble crystals
Lead chloride ($PbCl_2$): white needles, very sparingly soluble
Lead sulfate ($PbSO_4$): an insoluble white crystalline powder
Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$: a soluble white salt called *sugar of lead*
Lead chromate ($PbCrO_4$): used as a pigment in paint (*chrome yellow*)

Paints. A paint consists of three essential ingredients: the vehicle, the body, and the pigment.

1. ***The vehicle, or liquid medium.*** This must be an oil which will dry rapidly and harden in drying to a more or less flexible, hornlike body. These changes in the oil are due to oxidation by the air. A number of different oils will serve this purpose, but linseed oil has long been used as the standard drying oil, since it can be produced in quantity and at moderate cost. It is customary to add to it a *dryer*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation.

2. ***The body.*** The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries, and will have good covering power. While white lead meets these requirements, it is moderately expensive and it also blackens when exposed to hydrogen sulfide, which is likely to be present in the air in cities. Other bodies are now frequently combined with the lead, or replace it altogether, among them being zinc oxide, China clay (or kaolin),

barium sulfate, and a product called lithopone (p. 448). For some purposes these materials are a real advantage, and they are not to be regarded as adulterants unless sold as white lead.

3. ***The pigment, or coloring matter.*** In the case of white paints the body serves also as the coloring matter. For other colors a specific pigment must be added. In most cases these pigments are metallic oxides or salts and are frequently natural products. Sometimes they are prepared by precipitating an amorphous body (usually a colloid) in the presence of an organic dye, the dye being absorbed by the precipitate and giving it a color. Such pigments can be prepared in an endless variety of colors and are called *lakes*. They are usually not so permanent as mineral pigments.

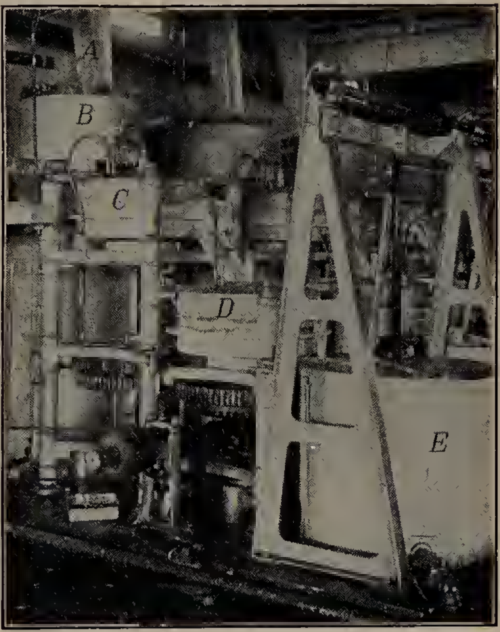


Fig. 202. Factory appliances used in mixing and grinding paint

Fig. 202 represents the method of manufacture of paint. The body, together with a little oil, enters at *A* and is ground in succession in *B*, *C*, *D*, and *E*, during which process the requisite amounts of oil, dryer, and pigment are added.

Storage cell. The storage cell, or accumulator, plays an important part in modern electrical developments. Its fundamental characteristic is that the chemical action upon which it depends is reversible. The chemical action taking place when the cell is delivering current is reversed when a current is conducted through the cell in an opposite direction. Electrical energy can therefore be stored in the cell as chemical energy and drawn off again, when desired, as electrical energy.

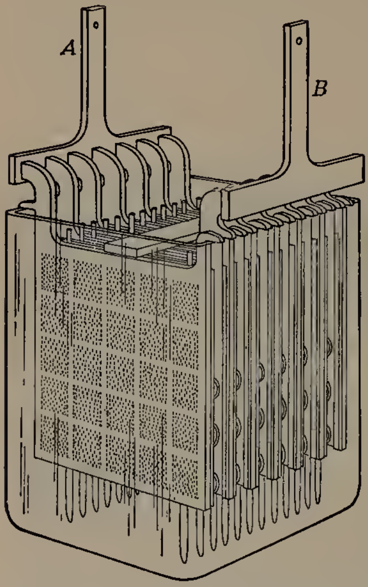


Fig. 203. A seven-plate storage battery

In the ordinary accumulator (Fig. 203) the electrodes are made of a skeleton of lead. When ready for use the one plate (*A*) is covered with a thick deposit of spongy lead, which is the active material; the other (*B*) is similarly covered with a layer of lead dioxide. The electrolyte is moderately dilute sulfuric acid. A number of pairs of such plates are arranged together in one cell. When the plates are connected by a wire the reaction is as follows:

$$\underset{(\text{Discharge} \longrightarrow)}{Pb + PbO_2 + 2\,H_2SO_4} \rightleftarrows \underset{(\longleftarrow \text{Charge})}{2\,PbSO_4 + 2\,H_2O}$$

It will be seen that the discharge of the cell results in bringing the two plates to an identical condition and in withdrawing sulfuric acid from the electrolyte. The cell is never allowed to come entirely to this discharged condition. When the current is reversed the two plates are restored to their original state.

Thorium and cerium. These elements are found in a few rare minerals, especially in the monazite sand of the Carolinas and Brazil. The oxides of these elements are used in the preparation of the Welsbach mantles for gas lights (p. 312) because of the intense light given out when a mixture of the oxides is heated. These mantles contain the oxides of cerium and thorium in the ratio of about 1 per cent of the former to 99 per cent of the latter. Compounds of thorium, like those of radium, are found to possess radioactivity, but in a less degree.

EXERCISES

1. How could you detect lead if present in tin foil?

2. Stannous chloride reduces gold chloride ($AuCl_3$) to gold. Give the equation.

3. What are the products of hydrolysis when stannic chloride is used as a mordant?

4. How could you detect arsenic or copper in lead?

5. Why is lead so extensively used for making water pipes?

6. What sulfates other than lead sulfate are insoluble?

7. Could lead nitrate be used in place of barium chloride in testing for sulfates?

8. How much lead peroxide could be obtained from 1 kg. of minium?

9. The purity of white lead is usually determined by observing the volume of carbon dioxide given off when it is treated with an acid. On the supposition that it has the formula $2\,PbCO_3 \cdot Pb(OH)_2$, how nearly pure was a sample if 1 g. gave 30 cc. of carbon dioxide at 20° and 750 mm.?

10. Silicon belongs in the same family with tin and lead. In what respects are these elements similar?

11. What weight of tin could be obtained by the reduction of 1 ton of cassiterite?

12. What reaction would you expect to take place when lead peroxide is treated with hydrochloric acid?

13. White lead is often adulterated with barytes. Suggest a method for detecting it, if present, in a given example of white lead.

14. Sugar of lead may be prepared by treating litharge with acetic acid. What weight of litharge is necessary for the preparation of 1000 g. of sugar of lead?

CHAPTER XLI

MANGANESE AND CHROMIUM

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF ACIDS
Manganese	Mn	54.93	8.01	1260°	H_2MnO_4 and $HMnO_4$
Chromium	Cr	52.00	7.3	1520°	H_2CrO_4 and $H_2Cr_2O_7$

General. Manganese and chromium, while belonging to different families, have so many features in common in their chemical conduct that they may be studied together with advantage. They differ from most of the elements so far studied in that they can act either as *base-forming* or as *acid-forming* elements. As base-forming elements each of the metals forms two series of salts. In the one series the metal is bivalent, and in the other series it is trivalent. The acids in which these elements play the part of a non-metal are unstable, but their salts are usually stable, and some of them are important compounds.

Elements like manganese and chromium, which in elementary form have all the properties of metals but which are capable of forming acids in higher states of valence, are called *metallo-acid* elements.

MANGANESE

Occurrence. Manganese is found in nature chiefly as the dioxide MnO_2, called *pyrolusite.* In smaller amounts it occurs as the oxides Mn_2O_3 and Mn_3O_4 and as the carbonate $MnCO_3$. Some iron ores also contain manganese.

Preparation and properties. The element is difficult to prepare in pure condition and has no commercial applications. It can be prepared, however, by reducing the oxide with aluminium powder (p. 455) or by the use of the electric furnace, with carbon as the reducing agent. The metal somewhat resembles iron in appearance, but is harder, more fusible, and more readily acted upon by air and moisture. Acids readily dissolve it, forming manganous salts.

By the reduction of a mixture of the oxides of iron and manganese an alloy is obtained known as *ferromanganese.* This is used very extensively as a purifier in making steel. About 14 lb. of manganese is used for every ton of steel produced.

Oxides of manganese. The following oxides of manganese are known: MnO, Mn_2O_3, Mn_3O_4, MnO_2, and Mn_2O_7. Only one of these, the dioxide, needs special mention.

Manganese dioxide (pyrolusite) (MnO_2). This substance is the most abundant manganese compound found in nature, and is the ore from which all other compounds of manganese are made. It is a hard, brittle, black substance which is valuable as an oxidizing agent. It will be recalled that it is used in the laboratory preparation of chlorine and oxygen, in decolorizing glass which contains iron, and in the manufacture of ferromanganese.

Compounds containing manganese as a base-forming element. As has been stated previously manganese forms two series of salts. The most important of these salts, all of which belong to the *manganous* series, are the following:

Manganous chloride	$MnCl_2 \cdot 4\,H_2O$
Manganous sulfide	MnS
Manganous sulfate	$MnSO_4 \cdot 4\,H_2O$
Manganous carbonate	$MnCO_3$
Manganous hydroxide	$Mn(OH)_2$

The chloride and the sulfate may be prepared by heating the dioxide with hydrochloric and sulfuric acids respectively:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2$$
$$2\,MnO_2 + 2\,H_2SO_4 \longrightarrow 2\,MnSO_4 + 2\,H_2O + O_2$$

The sulfide, carbonate, and hydroxide, being insoluble, may be prepared from a solution of the chloride or the sulfate by precipitation with the appropriate reagents. Most of the manganous salts are rose colored. They not only have formulas similar to the ferrous salts but resemble them in many of their chemical properties.

Compounds containing manganese as an acid-forming element. Manganese forms two unstable acids; namely, manganic acid (H_2MnO_4) and permanganic acid ($HMnO_4$). While these acids are of little interest, some of their salts, especially the permanganates, are important compounds.

Manganic acid and manganates. When manganese dioxide is fused with an alkali and an oxidizing agent a green compound is formed. The equation, when caustic potash is used, is as follows:

$$MnO_2 + 2\,KOH + [O] \longrightarrow K_2MnO_4 + H_2O$$

The green compound, K_2MnO_4, is called potassium manganate and is a salt of the unstable manganic acid. The manganates, as well as the free acid, are all very unstable.

Permanganic acid and the permanganates. When potassium manganate is treated with water a reversible decomposition takes place which can be expressed by the equation

$$3\,K_2MnO_4 + 4\,H_2O \rightleftarrows 2\,KMnO_4 + Mn(OH)_4 + 4\,KOH$$

If an acid is now added the potassium hydroxide is neutralized and the reaction goes on to completion, the chief product being *potassium permanganate*, $KMnO_4$. Since one third of the manganese is lost in this reaction, potassium permanganate is now made by electrolysis. The manganate is dissolved in water, and at the anode the oxygen evolved by the electrolysis of water acts upon the manganate in the following way:

$$2\,K_2MnO_4 + H_2O + [O] \longrightarrow 2\,KMnO_4 + 2\,KOH$$

Potassium permanganate crystallizes in dark-purple needles and is very soluble in water, forming an intensely purple solution. All other permanganates, as well as permanganic acid itself, are very soluble and give solutions of the same color. Unfortunately sodium permanganate ($NaMnO_4$) is very difficult to crystallize, so that the cheaper sodium cannot be used to replace potassium in this salt.

Oxidizing properties of the permanganates. The permanganates are remarkable for their strong oxidizing properties. When used as an oxidizing agent the permanganate is itself reduced, the exact character of the products formed from it depending upon whether the oxidation takes place (1) in an alkaline or neutral solution or (2) in an acid solution.

1. ***Oxidation in alkaline or neutral solution.*** When the solution is either alkaline or neutral *the potassium and the manganese of the permanganate are both converted into hydroxides*, as shown in the equation

$$2\,KMnO_4 + 5\,H_2O \longrightarrow 2\,Mn(OH)_4 + 2\,KOH + 3\,[O]$$

2. ***Oxidation in acid solution.*** When free acid such as sulfuric acid is present *the potassium and the manganese are both changed into salts of the acid*:

$$2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O]$$

Under ordinary conditions, however, neither one of these reactions takes place except in the presence of a third substance which is capable of oxidation. The oxygen is not given off in the free state, as the equations show, but is used up in effecting oxidation.

Potassium permanganate is particularly valuable as an oxidizing agent not only because it acts readily either in acid or in alkaline solution but also because the reaction takes place so easily that often it is not even necessary to heat the solution to secure action. The substance finds many uses in the laboratory, especially in analytical work. It is also used as an antiseptic and a disinfectant.

CHROMIUM

Occurrence. The ore from which all chromium compounds are made is *chromite*, or chrome iron ore ($FeCr_2O_4$). This is found most abundantly in New Caledonia and Greece, while in the United States it is produced in California and Oregon. The element also occurs in small quantities in many other minerals, especially in crocoite ($PbCrO_4$), in which mineral it was first discovered.

Preparation and properties. Chromium, like manganese, is very hard to reduce from its ores, owing to its great affinity for oxygen. It can, however, be made by the same methods which have proved successful with manganese.

Chromium is a very hard metal of about the same density and melting point as iron. At ordinary temperatures air has little action on it; at higher temperatures, however, it burns brilliantly. Nitric acid has no action on it, but hydrochloric and dilute sulfuric acids dissolve it, liberating hydrogen and forming chromous salts.

Chromium is a valuable metal for producing certain steel alloys. For this purpose *ferrochromium* is first made by reducing chromite with carbon, and this is added to the liquid steel in quantities sufficient to produce the desired alloy. The metal also forms desirable alloys with other metals, such as copper and nickel.

Compounds containing chromium as a base-forming element. While chromium forms two series of salts, chromous salts are difficult to prepare in the solid state and are of little importance. The most important of the chromic series are the following:

Chromic hydroxide	$Cr(OH)_3$
Chromic sulfate	$Cr_2(SO_4)_3$
Chromic chloride	$CrCl_3 \cdot 6\ H_2O$
Potassium chrome alum	$KCr(SO_4)_2 \cdot 12\ H_2O$

Chromic hydroxide, $Cr(OH)_3$. This substance being insoluble can be obtained by precipitating a solution of the chloride or sulfate with a soluble hydroxide. It is a greenish substance which, like aluminium hydroxide, dissolves both in alkalies and in acids.

Dehydration of chromium hydroxide. When heated gently chromic hydroxide loses a part of its oxygen and hydrogen, forming the substance $CrO \cdot OH$, which, like the corresponding aluminium compound, has more pronounced acid properties than the hydroxide. It forms a series of salts very similar to the spinels; chromite is the ferrous salt of this acid, having the formula $Fe(CrO_2)_2$. When heated to a higher temperature chromic hydroxide is completely dehydrated, forming the trioxide Cr_2O_3. This resembles the corresponding oxides of aluminium and iron in many respects. It is a bright-green powder, the shade of green depending upon the exact conditions of preparation. Both the hydroxide and the oxide are used as green pigments.

Chromic sulfate, $Cr_2(SO_4)_3$. This compound is a violet-colored solid which dissolves in water, forming a solution of the same color. This solution, however, turns green when heated, owing to the formation of basic salts. Chromic sulfate, like ferric and aluminium sulfates, unites with the sulfates of the alkali metals to form alums, of which the best known are potassium chrome alum, $KCr(SO_4)_2 \cdot 12\,H_2O$ and ammonium chrome alum, $NH_4Cr(SO_4)_2 \cdot 12\,H_2O$. These form beautiful dark-purple crystals and have some practical uses in the tanning industry and in photography. A number of the salts of chromium are also used in the dyeing industry, for they hydrolyze like aluminium salts and the hydroxide forms a good mordant.

Hydrolysis of chromium salts. When ammonium sulfide is added to a solution of a chromium salt, such as the sulfate, chromium hydroxide is precipitated instead of the sulfide. This is due to the fact that chromic sulfide, like aluminium sulfide, hydrolyzes in the presence of water, forming chromic hydroxide and hydrogen sulfide. Similarly, a soluble carbonate precipitates a basic carbonate of chromium.

Compounds containing chromium as an acid-forming element. Like manganese, chromium forms two unstable acids, namely, chromic acid and dichromic acid. Their salts, the chromates and dichromates, are important compounds.

Chromates. When a chromium compound is fused with an alkali and an oxidizing agent a chromate is produced. When sodium hydroxide is used as the alkali the equation is

$$2\,Cr(OH)_3 + 4\,NaOH + 3\,[O] \longrightarrow 2\,Na_2CrO_4 + 5\,H_2O$$

This reaction recalls the formation of a manganate under similar conditions.

Properties of chromates. The chromates are salts of the unstable chromic acid (H_2CrO_4) and as a rule are yellow in color. Potassium chromate (K_2CrO_4) and sodium chromate (Na_2CrO_4) are freely soluble in water, but most of the chromates are insoluble and can be prepared by precipitation. Thus, when a solution of potassium chromate is added to a solution of lead nitrate or of barium nitrate, the reactions expressed by the following equations occur:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2\,KNO_3$$
$$Ba(NO_3)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2\,KNO_3$$

Lead chromate (chrome yellow) and barium chromate separate as yellow precipitates. The presence of either of these two metals can be detected by taking advantage of these reactions.

Dichromates. When sodium chromate or potassium chromate is treated with an acid, a salt of the unstable dichromic acid ($H_2Cr_2O_7$) is formed:

$$2\,Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The relation between the chromates and dichromates is the same as that between the phosphates and the pyrophosphates. Sodium dichromate might therefore be called sodium pyrochromate.

Until recent years potassium dichromate ($K_2Cr_2O_7$) has been the best-known dichromate and the most familiar chromium compound. It forms large crystals of a brilliant-red color and is rather sparingly soluble in water. Sodium dichromate is much more soluble in water than the potassium salt, and the crystals deposited from the saturated solution are not so well formed and are somewhat deliquescent. They have the formula $Na_2Cr_2O_7 \cdot 2\,H_2O$. The sodium salt is now more widely used than the potassium salt.

Properties and uses of dichromates. When a soluble dichromate is treated with a solution of a base the dichromate is converted into the chromate:

$$Na_2Cr_2O_7 + 2\,NaOH \longrightarrow 2\,Na_2CrO_4 + H_2O$$

When a solution of a dichromate is added to a solution of a lead or a barium salt the corresponding chromate (not dichromate) is precipitated. With barium nitrate the equation is

$$2\,Ba(NO_3)_2 + Na_2Cr_2O_7 + H_2O \longrightarrow 2\,BaCrO_4 + 2\,NaNO_3 + 2\,HNO_3$$

Sodium dichromate finds use in many industries as an oxidizing agent, especially in the preparation of organic substances, such as the dye alizarin. It is also used in preparing pigments and in the process of tanning.

Oxidizing action of chromates and dichromates. When a solution of a chromate or of a dichromate is treated with an excess of an acid, chromic acid is set free. With sodium dichromate and sulfuric acid the equation is as follows:

$$Na_2Cr_2O_7 + H_2SO_4 + H_2O \longrightarrow Na_2SO_4 + 2\,H_2CrO_4$$

If now there is some material present that is easily oxidized, the chromic acid acts as an oxidizing agent, the chromium being converted into a trivalent metal in the process. In the presence of sulfuric acid the equation may be written thus:

$$2\,H_2CrO_4 + 3\,H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 5\,H_2O + 3\,[O]$$

The oxygen is not given off as such, but is taken up by the substance undergoing oxidation. For example, with ferrous sulfate the equation is as follows:

$$6\,FeSO_4 + 3\,H_2SO_4 + 3\,[O] \longrightarrow 3\,Fe_2(SO_4)_3 + 3\,H_2O$$

The three equations showing the steps in the oxidizing action of sodium dichromate upon ferrous sulfate may be combined into one equation:

$$\begin{aligned}&Na_2Cr_2O_7 + 7\,H_2SO_4 + 6\,FeSO_4\\&\longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O\end{aligned}$$

It will be seen that a dichromate decomposes in very much the same way that a permanganate does, *the sodium and chromium being both changed into salts in which they play the part of metals*, while part of the oxygen is liberated.

Potassium chrome alum. When potassium dichromate and sulfuric acid are used for oxidation it will be noticed that potassium sulfate and chromium sulfate are formed as the products of the reaction. On evaporating the solution these substances crystallize out as potassium chrome alum, which substance is produced as a by-product in the industries using potassium dichromate for oxidizing purposes. Sodium does not form a similar alum.

Chromic anhydride (CrO_3). When concentrated sulfuric acid is added to a concentrated solution of potassium dichromate, and the liquid is allowed to stand, deep-red needle-shaped crystals appear which have the formula CrO_3. This oxide of chromium is called *chromic anhydride* since it combines readily with water to form chromic acid:

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

It is therefore analogous to sulfur trioxide, which forms sulfuric acid in a similar way:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Chromic anhydride is a very strong oxidizing agent, giving up oxygen and forming chromic oxide:

$$2\,CrO_3 \longrightarrow Cr_2O_3 + 3\,[O]$$

EXERCISES

1. How does pyrolusite effect the decolorizing of glass containing iron?

2. Write the equations for the preparation of manganous chloride, manganous carbonate, and manganous hydroxide.

3. Write the equations representing the reactions which take place when ferrous sulfate is oxidized to ferric sulfate by potassium permanganate in the presence of sulfuric acid.

4. In the presence of sulfuric acid, oxalic acid is oxidized by potassium permanganate according to the equation

$$C_2H_2O_4 + O \longrightarrow 2\,CO_2 + H_2O$$

Write the complete equation.

5. 10 g. of iron were dissolved in sulfuric acid and oxidized to ferric sulfate by potassium permanganate. What weight of the permanganate was required?

6. What weight of ferrochromium containing 40% chromium must be added to a ton of steel to produce an alloy containing 1% of chromium?

7. Write the equation representing the action of ammonium sulfide upon chromium sulfate.

8. Sodium chromate oxidizes hydrochloric acid, forming chlorine. Write the complete equation.

9. Give the action of sulfuric acid on sodium dichromate (*a*) in the presence of a large amount of water; (*b*) in the presence of a small amount of water.

10. What would be the percentage composition of ferrochromium made by reducing pure chromite?

11. What per cent of the total oxygen present in potassium dichromate is available as an oxidizing agent?

CHAPTER XLII

URANIUM; RADIUM AND THORIUM

Uranium. Uranium is a rare element whose compounds were first isolated from a mineral called *pitchblende* or uraninite, which is essentially an oxide of the formula U_3O_8. *Carnotite*, a mineral discovered more recently (1899), contains both uranium and vanadium and is found chiefly in Colorado and Utah. The carnotite ores are by far the most abundant source of uranium, the next in importance being the pitchblende deposits in Bohemia and Saxony. The American production of uranium ores is much greater than that of all other countries combined.

Compounds and uses. The most familiar compounds of uranium are the black oxide, U_3O_8, uranyl nitrate, $UO_2(NO_3)_2$, and sodium diuranate ($Na_2U_2O_7$). Most of the compounds of uranium are yellow or red. Their chief chemical use is in making greenish-yellow fluorescent glass, in the decorating of china with various shades of yellow, orange, and black, and in the making of orange-colored pigments. Uranium steel alloy has useful properties. It is said to be used for making heavy cannon, and to stand the heat and strain of rapid fire better than any other steel alloy.

Radioactivity of uranium. In 1896 the French physicist Becquerel discovered that uranium and all its compounds possess a property which has been named *radioactivity*. This radioactivity manifests itself in the following ways:

(1) A photographic plate wrapped in black paper and placed near a compound of uranium is affected as though exposed to light. A metallic object placed on the plate screens the plate from this action and leaves its outline on the plate when it is developed, forming a *radiograph* (Fig. 204). (2) A charged electroscope is rapidly discharged when any material containing uranium is brought near it, which shows that the air all about this material is an electrical conductor.

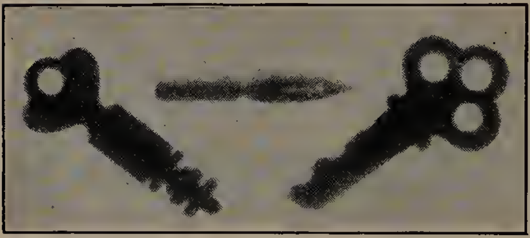


FIG. 204. A radiograph of some metal objects

Fig. 205 represents a simple form of aluminium-leaf electroscope, the leaves assuming the position indicated at *B* when an electric charge is communicated to the knob *A*. When a substance containing uranium (*C*, Fig. 206) is brought near the knob *A* the charge is rapidly lost, and the leaves collapse as shown at *B*.

The discovery of radium. Pitchblende was found to be four times as radioactive as uranium itself, which suggested that possibly there was some unknown element in the mineral that was carried over into the uranium salts as an impurity and was responsible for the radioactivity. Accordingly Monsieur and Madame Curie worked over the residues from a large quantity of pitchblende, and obtained a minute quantity of the chloride of a new element, which they named *radium*. This chloride is 3,000,000 times as active as uranium.

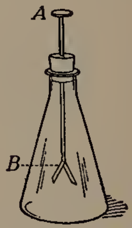


FIG. 205. A charged electroscope

The atomic weight of radium is 226.0, and this weight, as well as all of the other properties of the element and of its compounds, place it in the calcium family, just below barium. The metal itself was isolated by Madame Curie (Fig. 207) in 1910 and is very similar to barium.

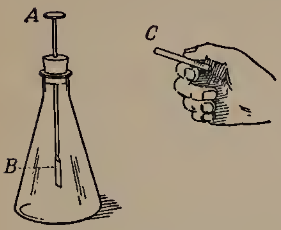


FIG. 206. A discharged electroscope

Quantity of radium available. Knowing the radioactivity of both uranium and radium, it is not difficult to estimate the proportion of radium in any ore containing uranium. Estimates of this kind bring to light a very surprising fact — the proportion of radium in all classes of uranium ores *is very constant*, and is about 1 part of radium in 2,940,000 parts of uranium. Probably not more than 50 g. or 60 g. of radium has been produced. In the form of the chloride, $RaCl_2$, it costs about $90,000 per gram.


FIG. 207. Madame Curie (1867–), Professor of physics in the University of Paris

Disintegration of radium. The extraordinary fact about radium is that although it is a well-characterized element, it is *slowly disintegrating*. In this process it is resolved into two other elements, one of which is *helium* and the other *niton*. These both belong in periodic Group 0 with the inactive gases of the atmosphere. Niton, in turn, decomposes into helium and still another element named radium A. Similar decompositions continue through a number of stages, and it is thought that the final product is *lead.*

In these decompositions two distinct kinds of particles are shot off with enormous velocity: (1) the one kind, called *alpha* (α) rays, consists of helium atoms charged positively and moving with a velocity about $\frac{1}{10}$ that of light; (2) the other, called *beta* (β) rays, consists of particles not more than $\frac{1}{1800}$ of the weight of a hydrogen atom and negatively charged. These are usually called *electrons*, and their initial velocity is nearly that of light. There is a third type of radiation known as *gamma* (γ) rays which does not consist of material particles, but of waves in the ether like light. The gamma rays resemble very closely the X rays of the Crookes tubes, but are much more powerful.

The rate at which the decomposition of radium proceeds cannot be changed by any means that has yet been tried. It is not affected by very high temperature nor by the nature of the radium compound.

Demonstration of the three types of rays. The existence of three different types of rays can be demonstrated in the following way: A small quantity of material rich in radium is placed at the bottom of a hole bored in a piece of lead (*A*, Fig. 208). A photographic plate (*B*), protected from light, is fixed at some distance above the radium, and the poles of a magnet *C*, *C*, are arranged one on each side of the hole in *A* and somewhat above it. The rays from the radium are shot out of the hole like bullets from a rifle. The positively charged alpha rays are bent out of their course by the attraction of the negative pole, while the negatively charged beta rays are bent in the opposite direction and to a much greater extent by the attraction of the positive pole. The gamma rays are not deflected at all. By developing the photographic plate the extent of deflection of the alpha and beta rays can be measured, and from such measurements it is possible to arrive at conclusions as to the relative masses and charges of the two kinds of particles.

Origin of radium. Radium is decomposing at a rate which places its average life at 2500 years, yet it is found in ores which are undoubtedly much older than this. It must therefore be in the process of formation from some other element. Experiment leaves no doubt that this element is *uranium*. The quantity of radium so constantly present in ores of uranium simply represents the equilibrium between the rate at which uranium disintegrates and that at which radium disintegrates. If this is the case, it is clear that we can never hope to find any deposits of radium richer than those afforded by uranium ores.

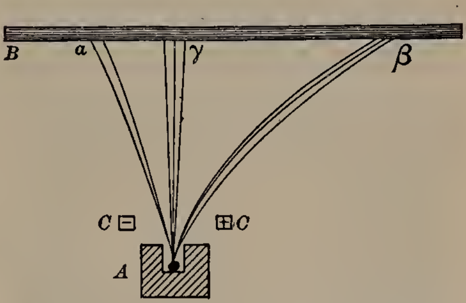


Fig. 208. The three types of rays emitted by radioactive substances

Energy of radium. During the decomposition of radium, niton, and the succeeding products a very great deal of energy is given off. Both the helium atoms and the electrons are shot off with very high kinetic energy, and the radium compound is kept heated by the heat energy set free. It is estimated that 1 gram of radium *hourly* evolves 132 calories of heat. From this value, together with the average life period (2500 years), it is easy to compute that the *total* energy given off by a gram of radium will be 250,000 times the heat of combustion of a gram of carbon. These unquestioned facts have thrown a great deal of doubt upon the older estimates of the age of the earth.

Radium and the atomic conception. It is clear that the atom of radium, as well as that of uranium, must have a very elaborate structure, since helium, electrons, and free energy are formed from them. All the facts in the case are brought into a fair degree of harmony if we assume that these atoms are made up (1) of a positive nucleus consisting of charged atoms of helium (and probably of hydrogen) closely packed together and constituting practically all the mass of the atom; and (2) a number of negative electrons revolving about the nucleus much as planets revolve about the central sun.

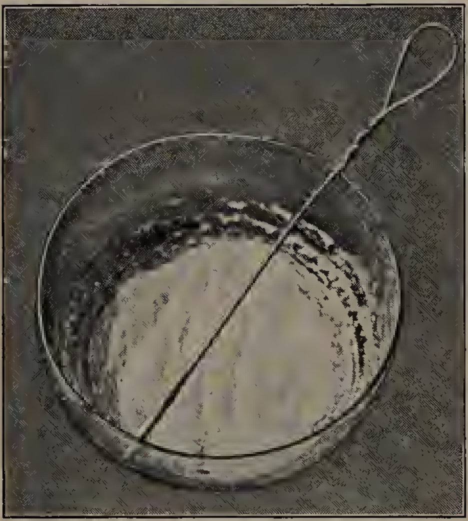


Fig. 209. Total quantity of radium bromide (1.764 g.) extracted from 300 tons of carnotite (actual size)

In the case of uranium and radium the system is unstable for some reason, and from time to time atoms explode expelling either electrons or atoms of helium, or both, and forming other atomic systems. The violent explosion causes an intense wave-motion in the ether that constitutes the gamma ray. In the case of most of the elements the atoms are stable, but they are probably made up of systems similar to the ones described.

This conception, which has many facts to support it, affords us some insight into the meaning of the periodic law, for the mass of any given atom will depend upon the number and character of the simple atoms constituting the nucleus.

The use of radium in the treatment of disease. The rays emitted from radium, niton, and other radioactive elements produce many chemical and physiological effects. They disintegrate glass, water, and many other substances. They produce severe burns upon the skin, like those of X rays. They kill bacteria and other microörganisms.

This latter property has led to the hope that exposure to the radiations of radium compounds might prove to be of assistance in effecting a cure for some diseases of the skin and for cancer. It is not possible as yet to say to what extent these hopes will be realized. Certain forms of cancer have apparently been cured in this way.

Radioactive thorium. The rare element *thorium* exhibits properties very similar to those of uranium. It gives rise to the same kind of series of radioactive elements by successive decomposition, producing the same varieties of radiation as the other series. Uranium and thorium are the elements of greatest atomic weight, and no other common elements are known to possess similar properties. This suggests the idea that possibly elements of still higher atomic weight may have existed at some time, but that they have disintegrated to form elements of smaller atomic weight which are not radioactive.

Disintegration series for uranium and thorium. Our knowledge of the stages in the disintegration of uranium and of thorium is more extensive than has been described in the account just given. The diagram (Fig. 210) prepared by Soddy gives a more complete summary of the

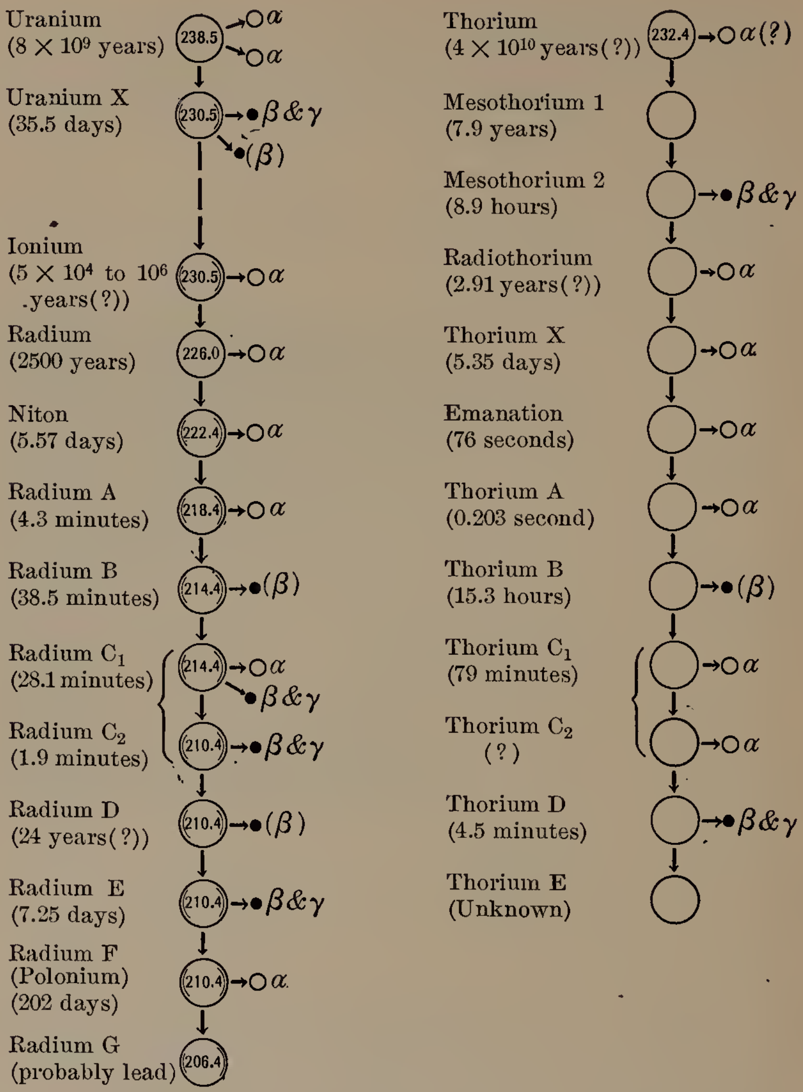


FIG. 210. Disintegration series for uranium and for thorium

name and atomic weight of the products formed, the average life of these products, and the character of the rays given out in the process of formation.

EXERCISES

1. When was uranium discovered, and how did it get its name? (See encyclopedia.)

2. For whom was carnotite named? (See dictionary.)

3. How is an electroscope charged? (See physics.)

4. What is the meaning of *alpha, beta,* and *gamma*?

5. What is the velocity of light? (See physics.)

6. How did thorium get its name? For what is the element used?

7. What weight of pitchblende is necessary for the preparation of 1 g. of radium?

CHAPTER XLIII

THE PLATINUM METALS AND GOLD

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	HIGHEST OXIDE	HIGHEST CHLORIDE	MELTING POINT
Ruthenium . .	Ru	101.7	12.26	RuO_4	$RuCl_4$	2450°
Rhodium . .	Rh	102.9	12.1	RhO_2	$RhCl_3$	1950°
Palladium . .	Pd	106.7	11.8	PdO_2	$PdCl_4$	1549°
Iridium . . .	Ir	193.1	22.42	IrO_2	$IrCl_4$	2350°
Osmium . . .	Os	190.9	22.47	OsO_4	$OsCl_4$	2700°
Platinum . .	Pt	195.2	21.50	PtO_2	$PtCl_4$	1755°
Gold	Au	197.2	19.30	Au_2O_3	$AuCl_3$	1063°

The family. Following iron, cobalt, and nickel in the eighth column of the periodic table are two groups of three elements each. The metals of the first of these groups — ruthenium, rhodium, and palladium — have atomic weights near 100 and densities near 12. The metals of the other group — iridium, osmium, and platinum — have atomic weights near 200 and densities near 21. These six rare elements have very similar physical properties and resemble each other chemically not only in the type of compounds which they form but also in the great variety of them. They occur closely associated in nature, usually as alloys of platinum in the form of irregular metallic grains in sand and gravel. They are known collectively as the platinum metals. Platinum and palladium are by far the most abundant of the six.

Although the periodic classification assigns gold to the silver-copper group, it much more closely resembles the platinum metals in its physical properties as well as in its chemical conduct, and it can be conveniently considered along with them. The four elements gold, platinum, osmium, and iridium are the heaviest substances known, being about twice as heavy as lead.

PLATINUM

Occurrence. About 90 per cent of the platinum of commerce comes from Russia, small amounts being produced in Colombia, New South Wales, Canada, and the United States. Owing to the rapidly increasing demands for the metal great efforts are being made to discover new deposits and a number of less important ones have been announced. Some ores of gold, copper, and nickel contain very small percentages of platinum, and this platinum is now recovered in the process of refining. In the United States about 24,500 oz. is now produced annually from this source, chiefly from blister copper and gold bullion.

Preparation. Native platinum is usually alloyed with gold and the platinum metals. To separate the platinum the alloy is dissolved in aqua regia, which converts the platinum into chloroplatinic acid (H_2PtCl_6). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate:

$$H_2PtCl_6 + 2\,NH_4Cl \longrightarrow (NH_4)_2PtCl_6 + 2\,HCl$$

Some iridium is also precipitated as a similar compound. On ignition the double chloride is decomposed, leaving the platinum as a spongy metallic mass, which is melted in an electric furnace and rolled or hammered into the desired shape.

Properties. Platinum is a grayish-white metal of high luster, and is very malleable and ductile. It melts in the oxyhydrogen blowpipe and in the electric furnace; it is harder than gold and is a good conductor of electricity. In finely divided form it has the ability to absorb or occlude gases, especially oxygen and hydrogen. These gases, when occluded, are in a very active condition resembling the nascent state, and can combine with each other at ordinary temperatures. A jet of hydrogen or coal gas directed upon spongy platinum is at once ignited.

Platinum as a catalytic agent. Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid. When desired for this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos.* The catalytic action seems to be in part connected with the property of absorbing gases and rendering them nascent. Some other metals possess this same power, notably palladium, which is remarkable for its ability to absorb hydrogen.

Chemical properties. Platinum is a very inactive element chemically, and is not attacked by any of the common acids. Aqua regia slowly dissolves it, forming platinic chloride ($PtCl_4$), which in turn unites with the hydrochloric acid present in the aqua regia, forming the compound chloroplatinic acid (H_2PtCl_6). Platinum is slowly attacked by fused alkalies. It combines at higher temperatures with carbon and phosphorus and alloys with many metals. It is readily attacked by chlorine, but not by oxidizing agents unless an alkali is present.

Applications. The applications of platinum in the sciences and the industries depend largely upon its high melting point, its chemical inactivity, and its malleability and ductility. It is extensively used (1) in scientific laboratories and in certain industries for evaporating pans, catalytic materials, and a great variety of laboratory appliances; (2) in electrical apparatus for contact points and, until recently, for lead-wires in the base of incandescent lamps; (3) in dentistry as pins for artificial teeth and as foil and plates in construction work; (4) in jewelry as a substitute for gold. Unfortunately the supply of the metal is very limited, and its cost is steadily advancing, so that it is now much more valuable than gold.

FIG. 211. Some laboratory utensils made of platinum

Platinum substitutes. To meet the serious shortage of platinum, efforts are being made to discourage its use in jewelry and to provide substitutes for other uses. Tungsten is taking its place for many purposes, especially for electrical spark contacts; wires of nickel iron coated with copper are now used in the manufacture of incandescent lamps; electrical-resistance heaters are made of alloys of nickel and chromium; quartz dishes are substituted for platinum in the industries; and a variety of alloys are being proposed for use in small laboratory utensils. Among these the following are the most promising at present:

Palau: an alloy of palladium (Pal) and gold (Au)
Rhotanium: an alloy of gold, palladium, and a small percentage of rhodium
Stellite: essentially an alloy of cobalt and chromium with some molybdenum or tungsten
Illium: essentially an alloy of nickel, chromium, copper, and molybdenum

The need of these substitutes can be seen from the following table of costs, which is, of course, subject to much change:

Platinum, per gram	$3.72
Palau, per gram	2.00
Gold, per gram	0.70

Compounds. Platinum forms two series of salts of which platinous chloride ($PtCl_2$) and platinic chloride ($PtCl_4$) are examples. Platinates are also known. While a great variety of compounds of platinum have been made, the substance is chiefly employed in the metallic state.

Chloroplatinic acid (H_2PtCl_6). When platinum is dissolved in aqua regia and the solution is crystallized, brownish-red crystals of the hydrate of chloroplatinic acid are obtained of the composition $H_2PtCl_6 \cdot 6\,H_2O$. The potassium and ammonium salts of this acid are nearly insoluble in water and alcohol. The acid is therefore used as a reagent to precipitate potassium in analytical work. With potassium chloride the equation is

$$2\,KCl + H_2PtCl_6 \longrightarrow K_2PtCl_6 + 2\,HCl$$

Other metals of the family. Of the other members of the family palladium is the most abundant. It occurs in considerable quantities alloyed with platinum in Brazil. It is also present in minute quantities in many ores of copper and nickel, and at present the chief source of palladium is the electrolytic muds of the nickel refineries.

Palladium is only about half as heavy as platinum, melts much lower, and is harder. It is used as a solder for platinum, for making graduated scales in scientific instruments, for making alloys, and as a substitute for platinum in jewelry. In the form of a powder it is a remarkably active catalytic agent.

Iridium gives a very hard alloy with platinum, used for pen points, compass bearings, and standard weights and measures.

Osmium tetroxide (OsO_4) is a very volatile liquid and is used under the name of osmic acid as a stain for sections in microscopy.

GOLD

Occurrence. Gold has been found in many localities, the most famous being South Africa, Australia, Russia, and the United States. In this country it is found in Alaska and in nearly half the states of the Union — notably in California, Colorado, and Nevada. It is usually found in the native condition, frequently alloyed with silver; in combination it is sometimes found as telluride ($AuTe_2$). The United States produces over one fifth of the world's annual output.

Mining and extraction. Native gold occurs in the form of small grains or larger nuggets in the sands of old rivers or imbedded in quartz veins in rocks. In the first case it is obtained in crude form by *placer* mining. The sand containing the gold is shaken or stirred in troughs of running waters called sluices. This sweeps away the sand but allows the heavier gold to sink to the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful streams of water delivered under pressure from pipes. This is called *hydraulic* mining. In *vein* mining the gold-bearing quartz is mined from the veins, stamped into fine powder in stamping mills, and the gold is extracted by a number of processes, two of which will be described.

1. ***Amalgamation process.*** In the amalgamation process the powder containing the gold is washed over a series of copper plates whose surfaces have been amalgamated with mercury. The gold sticks to the mercury or alloys with it, and after a time the gold and mercury are scraped off and the mixture is distilled. The mercury distills off and the gold is left in the retort ready for refining.

2. ***Cyanide process.*** This process depends upon the fact that gold is soluble in a solution of sodium cyanide in the presence of the oxygen of the air. The powder from the stamping mills is treated with a very dilute sodium cyanide solution which extracts the gold:

$$4\,Au + 8\,NaCN + 2\,H_2O + O_2 \longrightarrow 4\,NaOH + 4\,NaAu(CN)_2$$

From this solution the gold can be obtained by electrolysis or by precipitation with metallic zinc:

$$2\,NaAu(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2\,Au$$

Refining of gold. Gold is refined by three general methods:

1. ***Electrolysis.*** When gold is dissolved in a solution of potassium cyanide, and the solution electrolyzed, the gold is deposited in very pure condition on the cathode.

2. ***Cupellation.*** When the gold is alloyed with easily oxidizable metals, such as copper or lead, it may be refined by cupellation. The alloy is fused with an oxidizing flame

on a shallow hearth made of bone ash, which substance has the property of absorbing metallic oxides but not the gold. Any silver which may be present remains alloyed with the gold.

3. *Parting with sulfuric acid.* Gold may be separated from silver, as well as from many other metals, by heating the alloy with concentrated sulfuric acid. This dissolves the silver, while the gold is not attacked. Sometimes nitric acid is used instead of sulfuric acid.

Physical properties. Gold is a very heavy bright-yellow metal, exceedingly malleable and ductile, and a good conductor of electricity. It is quite soft and is usually alloyed with copper or silver to give it the hardness required for most practical uses. The degree of fineness is expressed in terms of carats, pure gold being twenty-four carats; the gold used for jewelry is usually eighteen carats, eighteen parts being gold and six parts copper or silver. Gold coinage is 90 per cent gold and 10 per cent copper.

Chemical conduct. Gold is not attacked by any of the common acids; aqua regia easily dissolves it, forming *chlorauric acid* ($HAuCl_4$). Fused alkalies also attack it. Most oxidizing agents are without action upon it, and in general it is not an active element.

Compounds. The compounds of gold, though numerous and varied in character, are of comparatively little importance and need not be described in detail. The element forms two series of salts in which it acts as a metal: in the aurous series the gold is univalent, the chloride having the formula $AuCl$; in the auric series it is trivalent, auric chloride having the formula $AuCl_3$. Gold also acts as an acid-forming element, forming such compounds as potassium aurate ($KAuO_2$). Its compounds are very easily decomposed, however, metallic gold separating from them.

EXERCISES

1. From the method of preparation of platinum, what metal is likely to be alloyed with it?

2. The "platinum chloride" of the laboratory is made by dissolving platinum in aqua regia. What is the compound?

3. How should you expect potassium aurate and platinate to be formed? What precautions would this suggest in the use of platinum vessels?

4. Why cannot gold be used for laboratory vessels instead of platinum?

5. What uses of platinum would seem to permanently lose it?

6. If platinum and palladium cost the same per ounce, which would be the more economical to use for jewelry?

7. An 18-carat gold ring weighs 5 g. What weight of chlorauric acid can be made from this?

CHAPTER XLIV

SOME APPLICATIONS OF THE RARER ELEMENTS

Rarer elements. A large number of elements are known which have not been described in the foregoing pages because an acquaintance with them is not at all necessary for an understanding of the principles of chemistry.

Some of these, while comparatively rare, could be produced in considerable quantities if there were any commercial use for them. A good example is *tellurium*, an element in the sulfur family obtained as a by-product in copper refining. Others of these elements are so rare that the cost of production is prohibitive, even though they have very useful properties.

Application in the industries. Some of these less familiar elements or their compounds have properties which make them valuable for special purposes, and mention of a few of these applications will be of interest.

The rare earths constitute a group of about sixteen elements, all trivalent and resembling aluminium in a general way. They are very difficult to separate from each other and always occur together in nature. Very large quantities of a mixture of them accumulate in the extraction of *thorium* from monazite sand (p. 312). The only one whose compounds are obtained pure rather easily is *cerium*. Compounds of cerium are used as mordants, as catalytic agents, and in medicine and photography. An alloy of cerium with iron is used as a gas or cigar lighter, since it gives off a stream of sparks when scratched by hard iron. Mixed salts of the other rare earths have been used as antiseptics, as mordants, and as pigments.

Thorium oxide, mixed with 1 per cent of cerium oxide, constitutes the material of which most gas mantles are made (p. 312).

Titanium in the silicon family is not a very rare element, occurring chiefly as the oxide TiO_2, called *rutile*, and as a constituent of certain iron ores (*ilmenite*). Large quantities of nearly pure titanium or of ferrotitanium are used in making steel rails designed to stand very heavy wear (railway curves and terminals). Titanium oxide is also incorporated in electric-arc carbons (*flaming* arc). Carbons thus made give a more diffused and efficient light than those made from pure carbon. The oxide is also used to impart a yellow color to glazes, to porcelain, and to artificial teeth.

Zirconium oxide is finding extensive use in the manufacture of fire-brick linings for furnaces and of tubes in which substances may be heated to a high temperature. Zircite contains 86 per cent ZrO_2, and zirconalba 99 per cent.

Vanadium occurs in considerable quantities in carnotite (p. 535) and in certain sulfides found in Peru. It is found as the oxide in the ash of nearly all anthracite coal. Ferrovanadium, like ferrotitanium, is used in producing special grades of steel, particularly when great toughness is desired (automobile parts). Its compounds are used as photographic developers, as catalytic reagents in the dye industry (aniline black), as coloring materials in glass, and as mordants.

Molybdenum compounds are used in coloring pottery and in dyeing silk, wool, and leather. Ammonium molybdate is an important reagent in the analysis of phosphates.

Ferromolybdenum has been used in making steel alloys, but does not seem to be superior to the cheaper ferrotungsten.

Tungsten compounds are produced in fairly large quantities. It has been found possible to draw the metal into very fine wire (0.3 mm.), which is now extensively used instead of carbon as a filament for incandescent lamps (Fig. 212). Its melting point is very high (3000°), and the consumption of electrical energy for a given candle power is so low that the lamp is about three times as efficient as the older (carbon) lamp. The metal is rapidly replacing platinum for electrical contacts in switches, telephone jacks, and automobile vibrators. Ferrotungsten is used in making steel designed for lathe tools, since such steel can be heated to a red glow without losing temper.

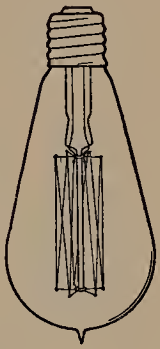


Fig. 212. A tungsten lamp

Compounds of tungsten are used for making fireproof cloth, and pigments for paints and pottery, and as mordants.

Selenium, an element in the sulfur family, is obtained as a by-product in refining copper. It is a nonconductor of electricity *when in the dark*, but becomes a fairly good conductor *when exposed to light.* This has led to its use in automatic fire alarms and for regulating automatic gas buoys at sea. Added to glass, it produces a fine red color, such glass being used for railway lanterns. It is also used to produce red enamels.

APPENDIX

CRYSTALLOGRAPHY

Crystals. When a liquid freezes it changes into a mass of solid bodies, each of which has a definite geometric form and is known as a *crystal.* Similar bodies may also be deposited from solutions or be formed by condensing vapors. Crystals are always bounded by plane surfaces, which are arranged in an orderly fashion with reference to imaginary lines drawn through the crystal and called its *axes.* Every crystal has therefore a definite geometric form. While the variety of form which crystals may assume is almost endless, it has been found that they may all be referred to one of six fundamental arrangements of axes, these constituting what are known as the *systems of crystallography.* These arrangements, together with two of the simplest crystal forms referred to each, are shown in the accompanying figures (Figs. 213–219).

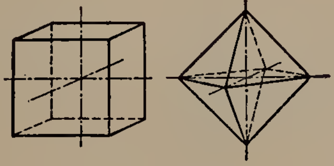


Fig. 213

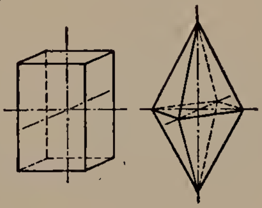


Fig. 214

The crystal systems. The relation of the axes in the several systems is as follows:

1. Isometric, or regular, system (Fig. 213): three equal axes all at right angles to each other.

2. Tetragonal system (Fig. 214): two equal axes and a third of different length, all at right angles.

3. Orthorhombic system (Fig. 215): three unequal axes all at right angles.

4. Monoclinic system (Fig. 216): two axes at right angles and a third at right angles to one of these but inclined toward the other. The axes may be of any relative lengths, and the angle of inclination may vary from 0° to 90°; but in a given substance both are constant.

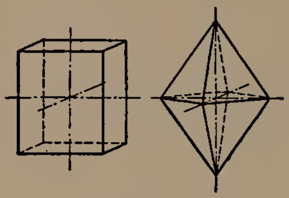


Fig. 215

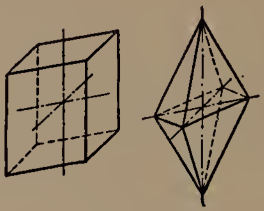


Fig. 216

5. Triclinic system (Fig. 217): three axes, all inclined toward each other. The axes may be of any relative length, and the angles of inclination may also vary.

6. Hexagonal system (Fig. 218): three equal axes in the same plane, intersecting at angles of 60°, and a fourth at right angles to all of these. In addition to the two general forms shown in Fig. 218 there are many rhombic forms belonging to this system (Fig. 219), and these are sometimes considered to constitute a seventh system.

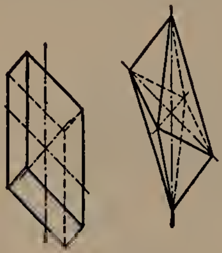


Fig. 217

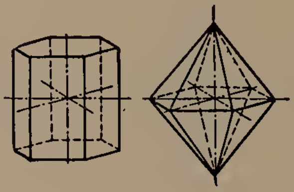


Fig. 218

Fig. 219

Structure of crystals. There is little doubt that these plans of formation correspond to orderly arrangements of the particles of solid matter of which the crystals are composed, so that the crystals resemble in structure the piles of cannon balls in a military park. In accordance with this idea it is known that the various properties of the crystal, such as hardness, strength, optical refraction, and conductivity toward heat and electricity, differ in different directions through the crystal. Crystals also split in definite directions, giving plane surfaces. Some of these groupings represent a more stable arrangement than do others, so that when a given substance crystallizes in two forms, as sometimes happens, the change from the one to the other is in general accompanied by an energy change. It is evident that a body like glass might be cut and polished so as to be an exact copy of a crystal, but would really not be one at all, since it would have none of the structure of a crystal.

Crystal form a characteristic of a substance. In general, under the same conditions, a given substance will always crystallize in a form which may be referred to the same system and with the same ratio of axis lengths and degree of inclination. The actual crystal form may be quite different, however. For example, the form may be either a cube or an octohedron, both of which are referred to the same axes. Not infrequently a substance may, under different conditions, assume two forms in entirely different systems, and it is then said to be *dimorphous.* For example, one form may occur when the substance freezes, and another when it is deposited from solution. Trimorphous substances are also known. When two substances crystallize in the same form and have the same inclination of axes and the same ratios in their lengths, they are said to be *isomorphous.*

Growth of crystals. When a substance starts to crystallize it usually happens that many small crystals form almost simultaneously. These small crystals then increase in size, and by choosing favorable conditions very large crystals may be secured. Slow growth favors the formation of large crystals, while rapid crystallization produces many small ones. The crystal is at all times in equilibrium with the liquid, some molecules dissolving from the crystal and others depositing upon it. For this reason an imperfect crystal often becomes perfect even though its weight is unchanged.

TABLES

TENSION OF AQUEOUS VAPOR AT VARIOUS TEMPERATURES, EXPRESSED IN MILLIMETERS OF MERCURY

Temperature	Pressure	Temperature	Pressure
0°	4.6	21°	18.62
16°	13.62	22°	19.79
17°	14.4	23°	21.02
18°	15.46	24°	22.32
19°	16.45	25°	23.69
20°	17.51	100°	760.00

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

Name	Weight of 1 Liter	Boiling Point	Name	Weight of 1 Liter	Boiling Point
Acetylene	1.1621	−83.8°	Hydrogen chloride	1.6398	−82.9°
Air	1.2928		Hydrogen fluoride	0.893	+19.4°
Ammonia	0.7708	−33.5°	Hydrogen sulfide	1.5392	−61.6°
Argon	1.7809	−186.0°	Methane	0.7168	−164.0°
Carbon dioxide	1.9768		Nitric oxide	1.3402	−153.0°
Carbon monoxide	1.2504	−190.0°	Nitrogen	1.2507	−195.7°
Chlorine	3.1674	−33.6°	Nitrous oxide	1.9777	−89.8°
Helium	0.1782	−268.7°	Oxygen	1.4290	−182.9°
Hydrogen	0.08987	−252.7°	Sulfur dioxide	2.9266	−8.0°

DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS

Name	Density	Melting Point	Name	Density	Melting Point
Aluminium	2.65	658.7°	Magnesium	1.74	651.0°
Antimony	6.52	630.0°	Manganese	8.01	1260.0°
Arsenic	5.73	850.0°	Mercury	13.56	−38.9°
Bismuth	9.80	271.0°	Nickel	8.9	1452.0°
Calcium	1.55	810.0°	Phosphorus	1.83	44.0°
Carbon, diamond	3.52		Platinum	21.50	1755.0°
Carbon, graphite	2.30	> 3600.0°	Potassium	0.862	62.3°
Chromium	7.3	1520.0°	Silicon	2.3	1420.0°
Cobalt	8.6	1480.0°	Silver	10.5	960.5°
Copper	8.93	1083.0°	Sodium	0.97	97.5°
Gold	19.32	1063.0°	Sulfur (rhombic)	2.06	112.8°
Iron	7.86	1530.0°	Tin	7.29	231.9°
Lead	11.37	327.4°	Zinc	7.10	419.4°

SOLUBILITY OF VARIOUS GASES IN WATER

Name of Gas	Volume absorbed at 0° and under 760 mm. Pressure by 1 Liter of Water
Ammonia	1298.9 liters
Hydrogen chloride	506.0 liters
Sulfur dioxide	79.79 liters
Hydrogen sulfide	4.37 liters
Carbon dioxide	1.713 liters
Oxygen	0.0496 liters
Hydrogen	0.0214 liters
Nitrogen	0.0233 liters

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

Substance	Formula	Weight dissolved by 100 cc. of Water at		
		0°	20°	100°
Calcium chloride	$CaCl_2$	59.5 g.	74.5 g.	159.0 g.
Sodium chloride	$NaCl$	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate	KNO_3	13.30 g.	31.6 g.	246.0 g.
Copper sulfate	$CuSO_4$	14.30 g.	21.7 g.	75.4 g.
Calcium sulfate	$CaSO_4$	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide	$Ca(OH)_2$	0.185 g.	0.165 g.	0.077 g.

RELATION OF COMMON UNITS AND METRIC UNITS

1 pound (troy) = 373.24 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.35 grams
1 United States quart = 0.946 liters
1 liter = 1.056 United States quarts
1 meter = 39.37 inches
1 centimeter = nearly $\frac{2}{5}$ inch
1 kilogram = nearly $2\frac{1}{5}$ pounds avoirdupois

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THE PERIODIC ARRANGEMENT OF THE ELEMENTS

Periods	Group 0		Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	
1	He = 3.99		Li = 6.94		Gl = 9.1		B = 11		C = 12.005		N = 14.01		O = 16		F = 19		
2		Ne = 20.2		Na = 23		Mg = 24.32		Al = 27.1		Si = 28.3		P = 31.04		S = 32.06		Cl = 35.46	
3	A = 39.88		K = 39.1		Ca = 40.07		Sc = 44.1		Ti = 48.1		V = 51		Cr = 52		Mn = 54.93		Fe = 55.84 Co = 58.97 Ni = 58.68
4				Cu = 63.57		Zn = 65.37		Ga = 69.9		Ge = 72.5		As = 74.96		Se = 79.2		Br = 79.92	
5	Kr = 82.92		Rb = 85.45		Sr = 87.63		Y = 89		Zr = 90.6		Cb = 93.5		Mo = 96				Ru = 101.7 Rh = 102.9 Pd = 106.7
6				Ag = 107.88		Cd = 112.4		In = 114.8		Sn = 118.7		Sb = 120.2		Te = 127.5		I = 126.92	
7	X = 130.2		Cs = 132.81		Ba = 137.37		La = Lu* 139.0 – 175.0		Ce = 140.25		Ta = 181.5		W = 184				Os = 190.9 Ir = 193.1 Pt = 195.2
8				Au = 197.2		Hg = 200.6		Tl = 204		Pb = 207.2		Bi = 208					
9	Nt = 222.4				Ra = 226				Th = 232.4				U = 238.2				
Formula of oxide Formula of hydride			R_2O RH		RO RH_2		R_2O_3 RH_3		RO_2 RH_4		R_2O_5 RH_3		RO_3 RH_2		R_2O_7 RH		RO_4

* This includes a number of elements whose atomic weights lie between 140 and 173, but which have not been accurately studied, and so their proper arrangement is uncertain. They do not fit into the table in its present form.

LIST OF THE ELEMENTS, THEIR SYMBOLS, AND ATOMIC WEIGHTS

O = 16

Aluminium 9	Al	27.1	Molybdenum 10	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.4	Palladium 9	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.90
Chlorine	Cl	35.46	Radium	Ra	226.00
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.10	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium 10	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium 10	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium 9	Ge	72.5	Sulfur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.2	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	89.3
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			